MEMOIRS
OF THE
RAMAN RESEARCH INSTITUTE

Vol. V
(Nos. 82 to 94)

BANGALORE
1957

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Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XLIII, No. 1, Sec. A, 1956

THE BIREFRINGENCE PATTERNS OF CRYSTAL SPHERES

BY SIR C. V. RAMAN
(*Memoir No. 82 of the Raman Research Institute, Bangalore 6*)

Received January 7, 1956)

THE preparation of polished spheres of crystalline solids is an ancient art, and indeed it is not uncommon to find large spheres of quartz as exhibits in natural history museums. Using appropriate techniques, it is possible to prepare spheres with different materials and of any desired size, even as small as half a centimetre in diameter. A spherical shape is evidently the most appropriate for a crystal to possess if we wish to observe or exhibit the variation of its optical properties with the direction of propagation of light over the entire possible range. Hence, a collection of such spheres is a useful acquisition for a crystallographic museum.

We may mention here as an example the case of the well-known pleochroic mineral iolite. Holding a polished sphere of this crystal so that it can be turned round and viewed against an extended source of light with a magnifier, Brewster's brushes can be seen around each of the two optic axes in the rear of the sphere. More generally, we place a crystal between a polariser and an analyser, *viz.*, two sheets of polaroid, and view it against an extended source of light. An arrangement should be provided for holding the sphere and altering its setting as desired. The birefringent pattern then seen in various settings shows at once whether the crystal is uniaxial or biaxial, whether the birefringence is weak or strong, whether the material is or is not optically active, and in the case of a biaxial crystal, what the angle between the optic axes is and how their positions vary with the wave-length of the light.

The plates accompanying the present paper illustrate some typical examples of such birefringent patterns. Plates I and II refer to the case of quartz in different settings, Plate III to beryl, Plate IV to calcite, Plate V to topaz, and Plate VI to the case of iolite already mentioned. The spheres used in this study were prepared at this Institute by Mr. J. Padmanabhan who also photographed the birefringence patterns, using for this purpose the monochromatic illumination furnished by a sodium vapour lamp. The principal difficulty encountered in the work was that of obtaining material for preparing the spheres which besides being of adequate size had also the

requisite degree of optical perfection. Any imperfections inevitably show up in the birefringence patterns. This is evident, for example, from the slight irregularities noticeable in the figures recorded for beryl and topaz in Plates III and V respectively.

By way of explanation of the observed effects, we may remark that a beam of light incident on a sphere and traversing it along a diameter would be brought to a focus at a point outside the sphere and at a distance from it depending upon the refractive index. Since there are two refractive indices for any given direction of propagation within a crystal, the positions of the two foci would be different except in the special cases when the direction of propagation within the crystal coincides with an axis of single-wave velocity. Hence, in all directions other than these axes the optical paths would be different for the two indices and interferences can therefore arise. The convergence of the light beams produced by the sphere would result in these interferences appearing in good focus on the surface of a sphere concentric with the crystal sphere but of larger diameter. Hence, when the sphere is rotated, the pattern would rotate with it, and its appearance as seen in any given direction would alter progressively.

With white light, the interferences in the vicinity of the axes of single wave-velocity exhibit colours. They are very fine in the case of calcite (Plate IV) but can be readily seen through a magnifier. These rings can also be seen with a magnifier in the case of topaz but not visible in the photographs of low magnification reproduced in Plate V. As seen through a magnifier, they appear unsymmetrically located with respect to the optic axes, evidently as the result of the dispersion of these axes.

Of a different nature are the circular or elliptic interference rings observed with the various crystals in directions very remote from the axes of single-wave velocity (see Figs. 5 and 6 in Plate I, Figs. 3, 4, 5 and 6 in Plate II, Figs. 5 and 6 in Plate III and Figs. 7 and 8 in Plate V). These interferences are only seen in monochromatic light and hence correspond to large differences of path between the two sets of waves which overlap.

Fig. 4 in Plate II is of special interest. It was recorded when the optic axis of the quartz sphere was set accurately parallel to the vibration direction of the polariser, the analyser also being accurately crossed with respect to it. It will be seen that the rings have not vanished even in this critical setting, but are faintly visible. Their visibility may be ascribed to the non-extinction of the transmitted light consequent on the optical activity of quartz in a direction transverse to the optic axis.

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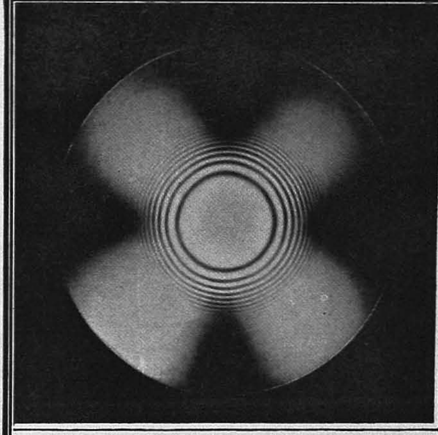

FIG. 1

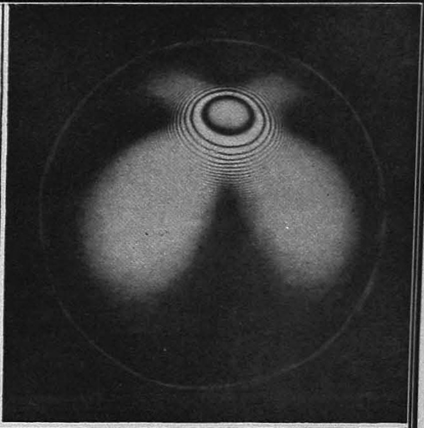

FIG. 2

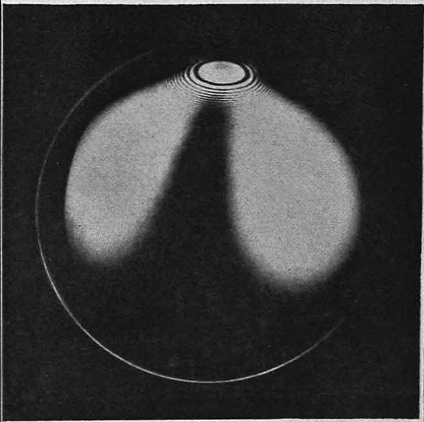

FIG. 3

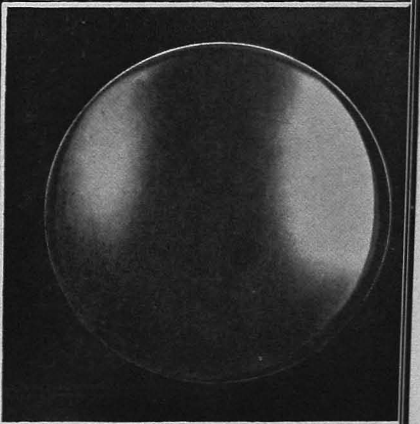

FIG. 4

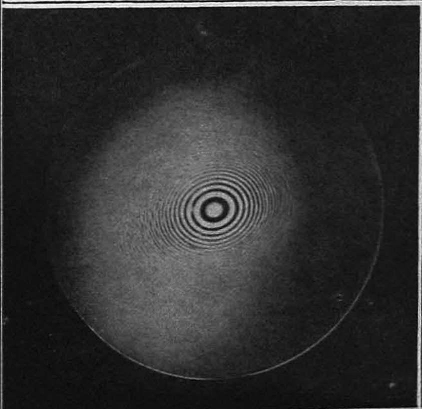

FIG. 5

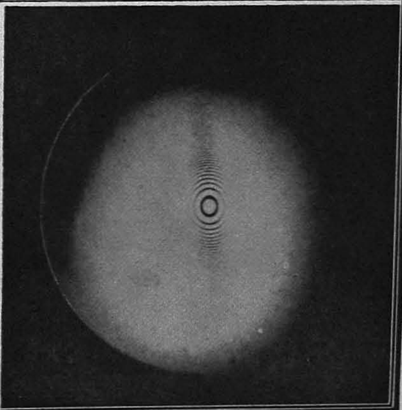

FIG. 6

Birefringence Patterns of Quartz Sphere

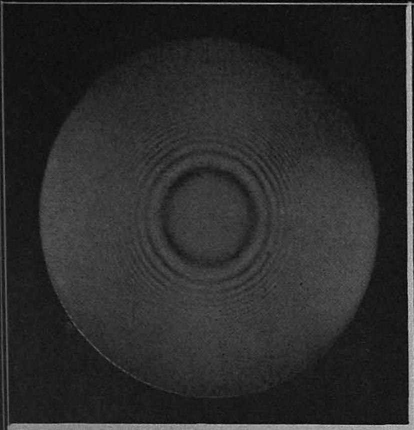

Fig. 1

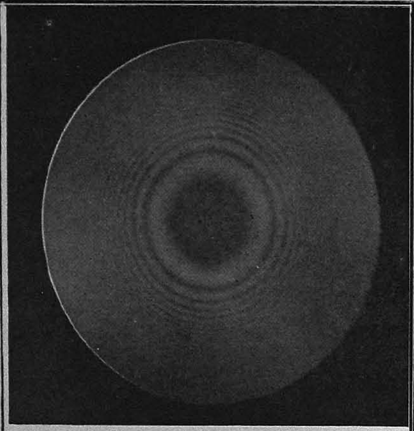

Fig. 2

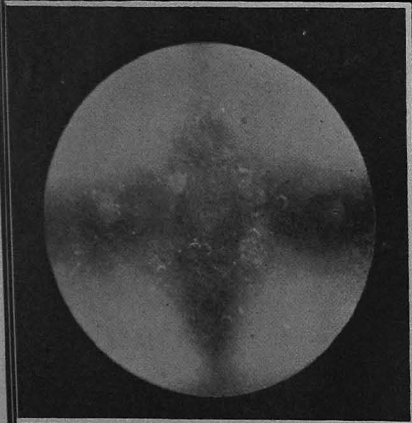

Fig. 3

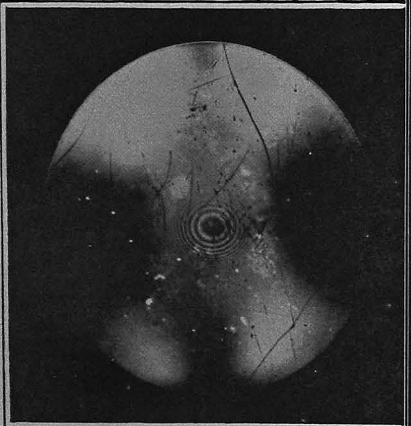

Fig. 4

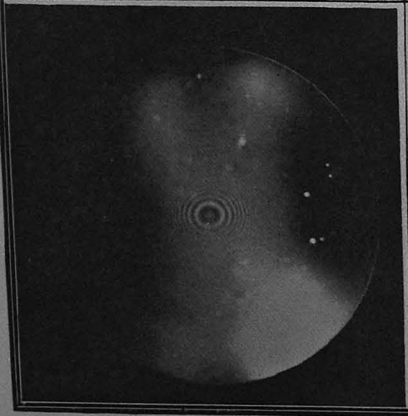

Fig. 5

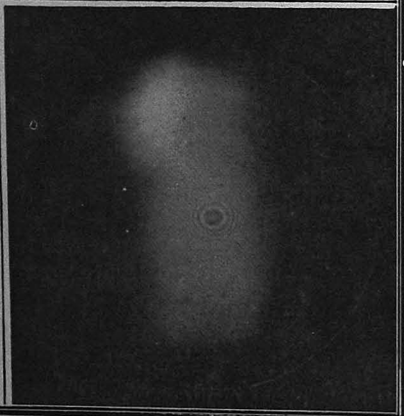

Fig. 6

Birefringence Patterns of Quartz Sphere

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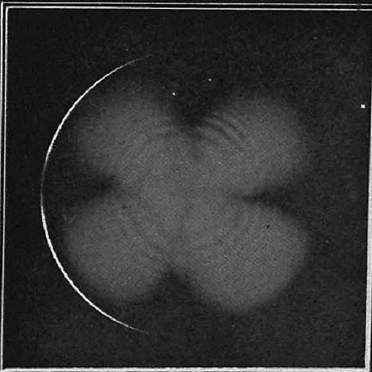

FIG. 1

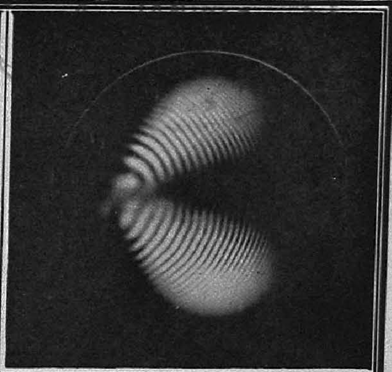

FIG. 2

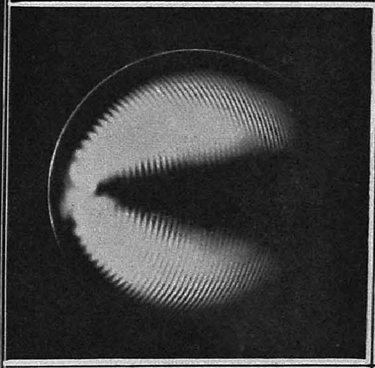

FIG. 3

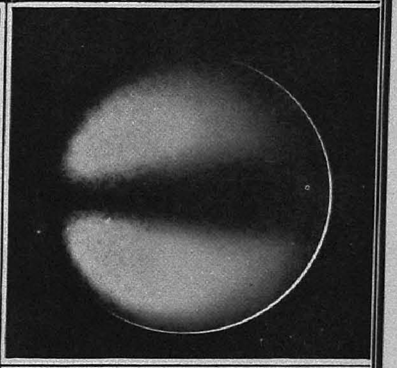

FIG. 4

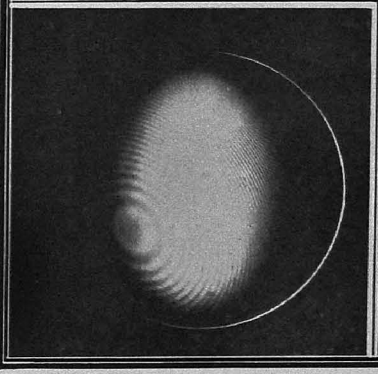

FIG. 5

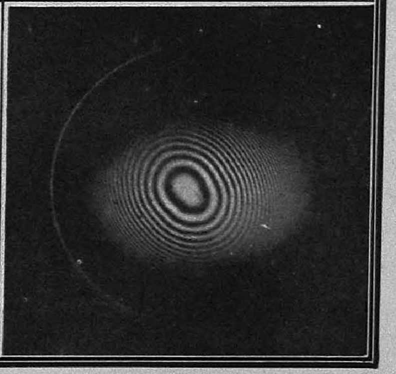

FIG. 6

Birefringence Patterns of BERYL Sphere

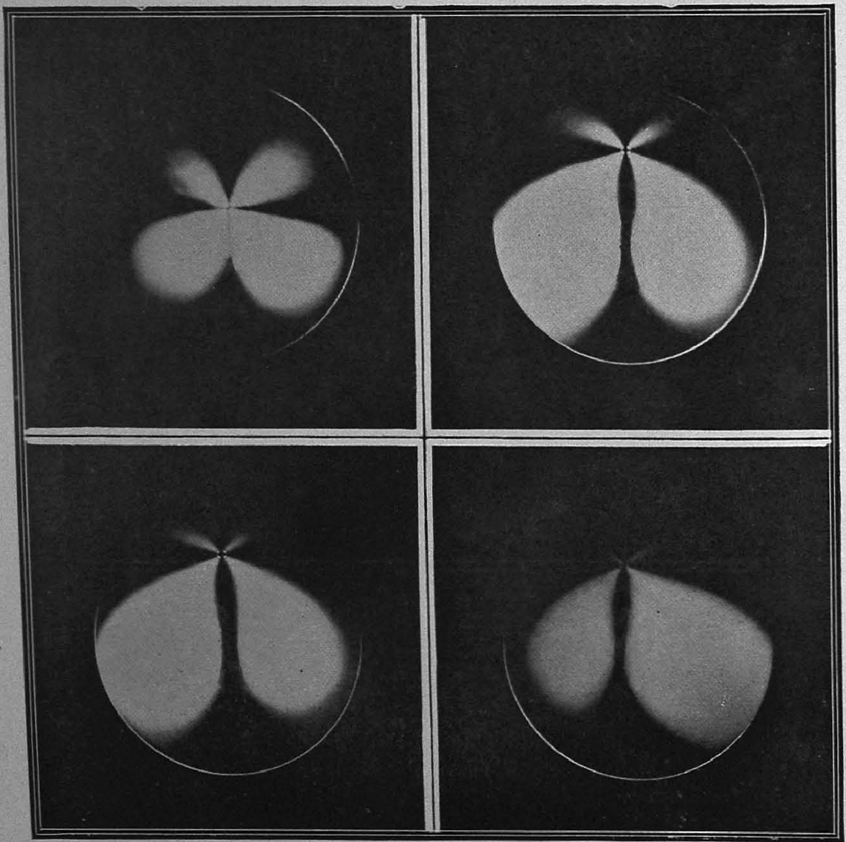

FIG. 1 FIG. 2

FIG. 3 FIG. 4

Birefringence Patterns of Calcite Sphere

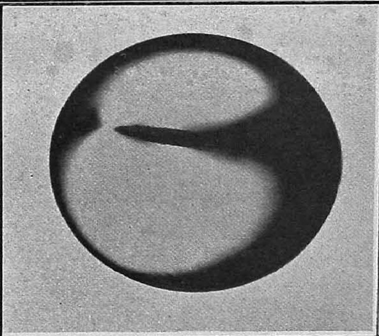

FIG. 1

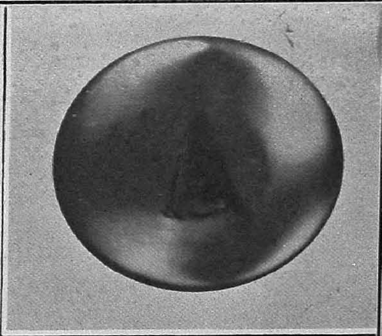

FIG. 2

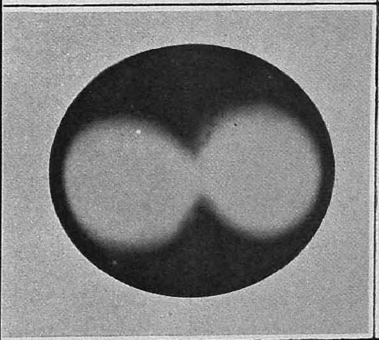

FIG. 3

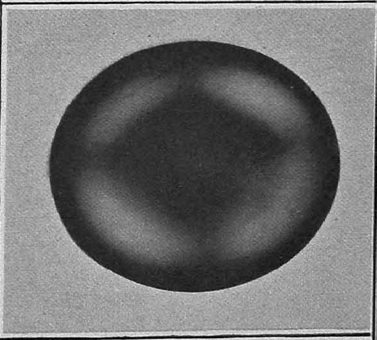

FIG. 4

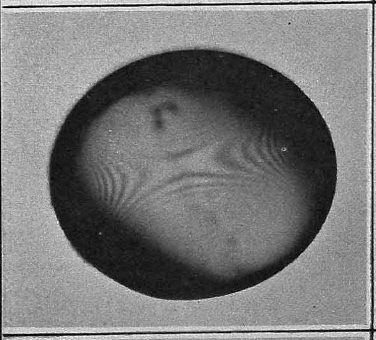

FIG. 5

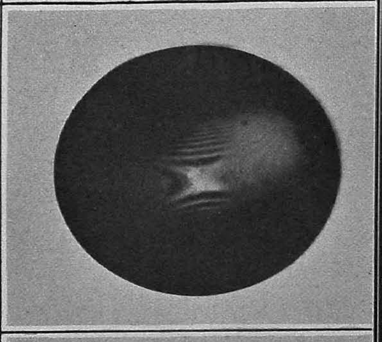

FIG. 6

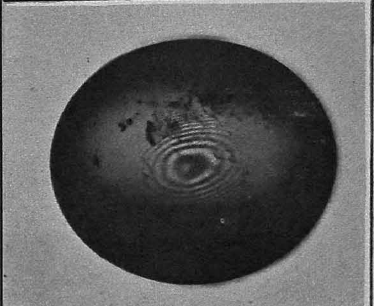

FIG. 7

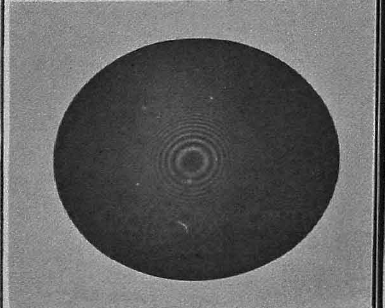

FIG. 8

Birefringence Patterns of Topaz Sphere

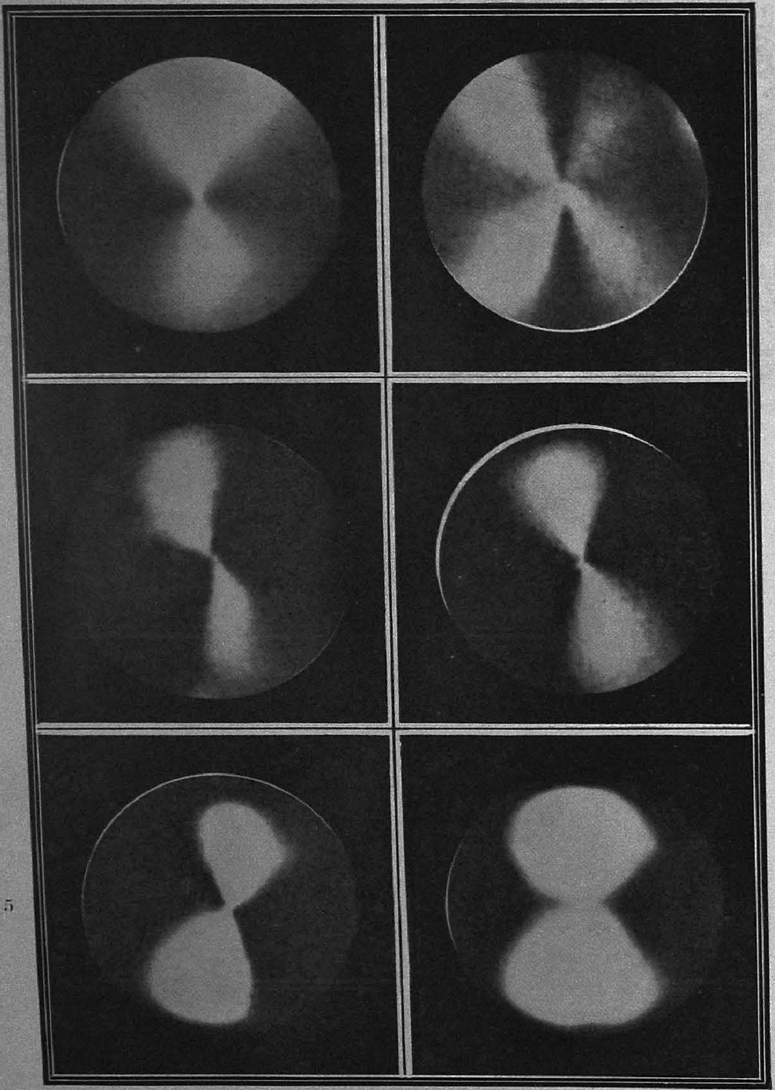

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

Birefringence Patterns of IOLITE Sphere

Fig. 1 in Plate VI represents Brewster's brushes as exhibited by iolite without any polariser or analyser. Similar brushes running parallel to them are also seen in the vicinity of the other axis of single-wave velocity. The other figures in Plate VI exhibit the effects of introducing either a polariser or an analyser, or both between the source of light and the eye of the observer.

SUMMARY

Light from an extended source traversing a sphere reaches foci lying on a concentric spherical surface of a larger radius determined by the refractive index. Hence, if the incident light be polarised and the sphere is viewed through an analyser, the interferences arising from the birefringence of the material are focussed by the sphere itself on such concentric surface and rotate with the sphere when the latter is rotated. Photographs of such patterns in typical cases are reproduced.

Reprinted from "The Proceedings of the Indian Academy of Sciences", Vol. XLIII, No. 4, Sec. A, 1956

ON THE PHENOMENOLOGICAL THEORY OF LIGHT PROPAGATION IN OPTICALLY ACTIVE CRYSTALS

BY S. PANCHARATNAM

(*Memoir No.* 83 *of the Raman Research Institute, Bangalore* 6)

Received March 14, 1956

(Communicated by SIR C. V. Raman)

1. INTRODUCTION

THE treatment customarily adopted[1] for analysing the propagation of light in optically active crystals is somewhat lengthy and cumbersome, and is even so not free from approximation: its mathematical complexity being perhaps partly the reason why an alternative quasi-theoretical analysis not involving the electromagnetic theory is sometimes used.[2,3] A concise yet logical treatment of the problem is, however, easily possible without the introduction of any fresh physical hypothesis—as will be shown in this paper.

We have merely to remember that for an electromagnetic wave inside a crystal, it is the dielectric displacement vector **D** (the 'vibration'), and not the electric intensity **E** which necessarily lies on the wave-front. Hence we seek to express **E** in terms of **D**, rather than *vice-versa*. Even for the case of optically inactive crystals, such a procedure—though not commonly adopted—is known to simplify the theoretical treatment, as may be seen especially in the case of absorbing crystals[4]; and the geometric representation of the optical properties of a crystal by an *index ellipsoid* follows directly in the structure of such a presentation instead of having to be proved by indirect means later—as is usually done.[5]

2. FORMULATION OF THE PROBLEM

Any wave travelling in the crystal along an arbitrary direction 'z' (conveniently taken as being normal to the plane of the paper) may be specified by giving the x and y components of the D-vibration: $D_x \exp i\omega(t - z/v)$ and $D_y \exp i\omega(t - z/v)$. Here v is the velocity of the wave and the ratio (D_y/D_x) completely defines the polarisation of the wave. Owing to the requirement that the vectors **D** and **E** must satisfy both Maxwell's relations as well as the characteristic polarisable property of the medium, only two specific waves can be propagated in the z-direction—the problem being to determine their velocities, v_1 and v_2, and their states of polarisation $(D_y/D_x)_1$ and $(D_y/D_x)_2$.

Maxwell's equations for a plane-wave field reduce to the following single equation when **H** is eliminated*—as is shown in standard texts[7]

$$v^2\mathbf{D} = c^2\,[\mathbf{E} - \mathbf{s}\,(\mathbf{E}.\mathbf{s})] \tag{1}$$

where **s** is a unit-vector along the wave-normal. For inactive crystals the polarisable characteristics of the medium lead to the usual relation $\mathbf{D} = (\epsilon)\,\mathbf{E}$, where (ϵ) represents the symmetric dielectric tensor—which operates on **E** to give **D**. But for optically active media it is assumed that

$$\mathbf{D} = (\epsilon)\,\mathbf{E} + i\,\mathbf{G}\times\mathbf{E} \tag{2}$$

where the additional antisymmetric term represents a feeble additional polarisation which oscillates out of phase with the electric intensity (as indicated by the factor i), and yet does not introduce any absorption because it is also orthogonal to the electric intensity (as is indicated by the occurrence of the vector product). The *gyration-vector* **G** corresponding to the direction of propagation **s** determines the optical rotatory power in that direction.

3. The Inverse Gyration-Vector

It is known that by taking the z-axis along the wave-normal (instead of choosing co-ordinate axes along the electrical axes, as in usual treatments), we not only confine ourselves to two components of **D** instead of three; in addition, the components of the vector equation (1) take the following intelligible form:

$$v^2\mathrm{D}_x = c^2\mathrm{E}_x;\ \ v^2\mathrm{D}_y = c^2\mathrm{E}_y;\ \ D_z = 0 \tag{1 a}$$

where, it may be noted, separate and explicit expressions are obtained for E_x and E_y.

Equation (2) which expresses **D** as a vector function of **E**, is now transformed by expressing **E** in terms of **D** using the inverse vector function. Since this inverse function will obviously contain not only a real symmetric part but also an imaginary antisymmetric part (giving that part of the electric intensity which oscillates out of phase with **D**, and is orthogonal to it), we may write

$$c^2\mathbf{E} = (a)\,\mathbf{D} - i\,\boldsymbol{\Gamma}\times\mathbf{D} \tag{2 a}$$

The first term alone would be present for an optically inactive crystal, the symmetric tensor (a) then defining the *index ellipsoid*†—being proportional to the inverse of the dielectric tensor (see Appendix). The comparatively

* We are not here considering other theories of optical activity[2,6] in which $\mathrm{B} \neq \mathrm{H}$.

† If $a_{11}x^2 + a_{22}y^2 + \ldots 2a_{31}\,zx = 1$, be the equation to the index ellipsoid, then the a_{ij} are also the components of the tensor (a) with respect to the co-ordinate axes chosen.

small second term (which introduces the optical activity) is determined by the new vector Γ—which we shall refer to as the inverse gyration-vector corresponding to the direction of propagation **s**.

4. Derivation of the Equations of Wave-Propagation

Writing down the x and y components of equation (2 a) and omitting the terms containing the factor D_z (since $D_z = 0$):

$$\left.\begin{aligned} c^2E_x &= a_{11}D_x + a_{12}D_y + i\Gamma_z D_y \\ c^2E_y &= a_{22}D_y + a_{12}D_x - i\Gamma_z D_x \end{aligned}\right\} \tag{3}$$

Here $a_{11}x^2 + a_{22}y^2 + 2a_{12}xy = 1$, is the equation to the elliptical section of the index ellipsoid taken perpendicular to the wave-normal. We now choose the x and y axes parallel to the principal radii of this elliptical section, which represent the vibration-directions in the absence of optical activity. *With this understanding* we may, in Equation (3), set $a_{12} = 0$, $a_{11} = v'^2$ and $a_{22} = v''^2$; here v' and v'' represent the velocities of the waves in the absence of optical activity, because of a well-known property of the index ellipsoid which may also be obtained by setting $\Gamma_z = 0$ at the end of the present discussion. Substituting for c^2E_x and c^2E_y from equation (1 a) we thus obtain as our fundamental equations:

$$\left.\begin{aligned} v^2 - v'^2 &= i\Gamma_z\left(\frac{D_y}{D_x}\right) \\ v^2 - v''^2 &= -\,i\Gamma_z\left(\frac{D_x}{D_y}\right) \end{aligned}\right\} \tag{4}$$

These fundamental equations are essentially the same as those obtained in Pockel's *Lehrbuch*[2] starting from an entirely different theory of optical activity. There are two pairs of roots v_1, $(D_y/D_x)_1$ and v_2, $(D_y/D_x)_2$, which simultaneously satisfy these equations—giving thereby the required velocities and states of polarisation.

5. The Velocities and States of Polarisation of the Waves

Multiplying the two equations of (4) to eliminate (D_y/D_x) we obtain the following quadratic in v^2, whose roots v_1^2 and v_2^2 give the velocities of the waves:

$$(v^2 - v'^2)(v^2 - v''^2) = \Gamma_z^2 \tag{5}$$

Subtracting the second equation of (4) from the first to eliminate v^2, we get;

$$\frac{D_y}{D_x} + \frac{D_x}{D_y} = i\frac{v'^2 - v''^2}{\Gamma_z} \tag{6}$$

This is a quadratic in (D_y/D_x), and its roots uniquely determine the states of polarisation because of the relation:

$$\frac{D_y}{D_x} = \frac{|D_y|}{|D_x|} e^{iR}$$

where the ratio $|D_y| : |D_x|$ is obviously the ratio $\tan\theta$ of the (real) amplitudes of the y and x components of the D-vibration; and R is the relative phase difference between these components. Since the right-hand side of (6) is entirely imaginary it follows that both roots of the equation are imaginary ($R = \pm \pi/2$). Further since the roots of (6) are obviously reciprocals of one another, it follows that if one root is of the form $(B_1/A_1)\, e^{i\pi/2}$, the other will be $(A_1/B_1)\, e^{-i\pi/2}$. This signifies that both vibrations are elliptically polarised with their respective major axes along the two perpendicular principal planes, the vibrations being of the same ellipticity but traced in opposite senses.

The value of $\tan 2\theta$, which determines the common ellipticity of the two vibrations is obtained directly from equation (6) by substituting in it the value of (D_y/D_x) which is equal to $(+\, i \tan\theta_1)$ for the right elliptic vibration and $(-\, i \tan\theta_2)$ for the left elliptic vibration:

$$|\tan 2\theta| = |2\Gamma_z/(v'^2 - v''^2)| \tag{7}$$

Similarly the difference in the squares of the velocities of the two waves may be obtained from (5)—since it is the square-root of the discriminant:

$$(v_1^2 - v_2^2) = (v'^2 - v''^2) + (2\Gamma_z)^2 \tag{8}$$

In the absence of linear birefringence (*i.e.*, if we imagine $v' = v''$), the waves will be circularly polarised according to (7), the rotatory power ρ being obtained from (8) as:

$$\rho = (\omega/v_m^3) \cdot \Gamma_z \tag{9}$$

where v_m is a mean velocity (see Pockels[2]).

We may mention that because of an approximation made in the usual treatment, its resultant equations differ slightly from (5) and (6); also, equations (7) and (8) are the accurate forms of the approximate relations obtained by the method of superposition.[2,3]

6. The Variation of Rotatory Power with Direction

The gyration vector **G**, and hence in the present treatment the inverse gyration-vector $\boldsymbol{\Gamma}$, are both vectors not having their axes fixed with respect to the crystallographic axes,‡ but are linear vector functions of the direction of propagation. Thus $\mathbf{G} = (g)\,\mathbf{s}$ and $\boldsymbol{\Gamma} = (\gamma)\,\mathbf{s}$, where the gyration tensor (g) and hence the modified gyration tensor (γ) are both nine-component tensors. The rotatory power is however determined, according to (9), only by the resolved component Γ_s of the inverse gyration-vector along the direction of propagation. (We are here denoting this by Γ_s instead of Γ_z since we are choosing an arbitrary co-ordinate system $x'y'z'$.) Since an analogous result holds in the usual treatment it follows as in that case[6] that this scalar parameter of rotation Γ_s is a quadratic function of the direction cosines $l'm'n'$ of propagation:

$$\Gamma_s = \gamma_{11}l'^2 + \gamma_{22}m'^2 + \gamma_{33}n'^2 + 2\bar{\gamma}_{12}l'm' + 2\bar{\gamma}_{23}m'n' + 2^{-}{}_{31}n'l'$$

where

$$\bar{\gamma}_{ij} = \tfrac{1}{2}(\gamma_{ij} + \gamma_{ji}), \qquad (i, j, = 1, 2, 3).$$

The discussion of optical activity in relation to crystal symmetry follows as in the usual treatment.

Finally, the author wishes to express his gratitude to Prof. Sir C. V. Raman, F.R.S., N.L., for his kind interest in this investigation.

7. Summary

In the usual treatment of the optical activity of crystals, the displacement vector of the light wave is expressed as a function of the electric vector—this being done with the aid of the dielectric tensor and the gyration-vector. The treatment is made more concise and tractable by using the inverse vector function and expressing the electric vector in terms of the displacement vector, since it is the latter which necessarily lies on the wave-front; this can be done by using the inverse of the dielectric tensor (which defines the index ellipsoid), and an inverse gyration-vector (which determines the rotatory power for the particular direction of propagation considered). The inverse gyration-vector (like the gyration-vector) is itself a function of the direction of propagation, being related to it by a modified gyration tensor—which consequently determines the rotatory power for all directions.

---

‡ The new treatment given in Sommerfeld's *Optics*[5] is deficient in this respect,

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APPENDIX

Since the index ellipsoid defined by the tensor (a), and the inverse gyration-vector Γ may be directly taken as the phenomenological quantities required to describe the propagation along any particular direction **s**, the relation between Γ and the gyration-vector **G** would not usually be required. The relation may however be obtained by writing (2) as $\mathbf{D}=\mathbf{D}' + i\mathbf{P}''$, where

$$\mathbf{D}' = (\epsilon)\,\mathbf{E};\ \ \mathbf{P}'' = \mathbf{G}\times\mathbf{E} \tag{11}$$

Substituting for **D** in (2 *a*)

$$c^2\mathbf{E} = (a)\,\mathbf{D}' + \Gamma\times\mathbf{P}'' + i\,(a)\mathbf{P}'' - i\Gamma\times\mathbf{D}'$$

Equating real parts and neglecting $\Gamma\times\mathbf{P}''$ in comparison with $c^2\mathbf{E}$:

$$(a) = c^2\,(\epsilon)^{-1} \tag{12}$$

Equating imaginary parts: $(a)\,\mathbf{P}'' = \Gamma\times\mathbf{D}'$. Choosing axes of co-ordinates X, Y, Z, along the principal electrical axes of the crystal, the X-component of this relation is

$$a_X P_X'' = \Gamma_Y D_Z' - \Gamma_Z D_Y'$$

or, by virtue of (11), if ϵ_X, ϵ_Y, ϵ_Z, be the principal dielectric constants,

$$a_X\,(G_Y E_Z - G_Z E_Y) = \Gamma_Y\,(\epsilon_Z E_Z) - \Gamma_Z\,(\epsilon_Y E_Y)$$

We may separately equate the coefficients of E_Y and E_Z occurring on both sides since this relation has to hold not just for *one* value of the ratio E_Y/E_Z, there being *two* polarised waves that can be propagated along the same direction. Hence, using (12),

$$\Gamma_Y = \frac{c^2}{\epsilon_Z\epsilon_X}\,G_Y;\ \ \Gamma_Z = \frac{c^2}{\epsilon_X\epsilon_Y}\cdot G_Z;\ \ \Gamma_X = \frac{c^2}{\epsilon_Y\epsilon_Z}\cdot G_X \tag{13}$$

The relation between the components of the modified gyration tensor and those of the gyration tensor may now be easily written down:

$$\gamma_{1i} = \frac{c^2}{\epsilon_Y\epsilon_Z}\,g_{1i};\ \ \gamma_{2i} = \frac{c^2}{\epsilon_Z\epsilon_X}\,g_{2i};\ \ \gamma_{3i} = \frac{c^2}{\epsilon_X\epsilon_Y}\,g_{3i} \qquad (i = 1, 2, 3).$$

ERRATA

On page 250, No. 4 of this Volume, Equation (8) should read as follows:—

$$(v_1^2 - v_2^2)^2 = (v'^2 - v''^2)^2 + (2\,\Gamma_z)^2$$

Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XLIII, No. 4, Sec. A, 1956

RAMAN SPECTRUM OF MAGNESITE

By D. Krishnamurti
(*Memoir No.* 84 *from the Raman Research Institute, Bangalore* 6)
Received March 17, 1956
(Communicated by Sir C. V. Raman)

1. Introduction

According to Dana,[1] magnesite ($MgCO_3$) commonly occurs in massive and compact forms but clear single crystals are rare. It is not surprising therefore that few investigations have been made on its Raman spectrum. The only study reported in the literature was by Schæfer and others[2] who, using a single crystal, have reported a line at a frequency shift of 1096 cm.$^{-1}$ The opportunity for the present study arose due to the fact that some clear crystals from Brumadas, Bahia, Brazil were made available to us through the kindness of Dr. C. S. Pichamuthu. The density of a clear specimen was determined and found to be 3·02 gm./c.c., in fair agreement with the value 3·037 given in the *International Critical Tables.*

As the specimens were colourless, it was thought that the complete Raman spectrum could be readily recorded using the λ 2536·5 resonance line of mercury for excitation. Actually however, the crystals were found to be opaque to radiations of shorter wave-length than λ 2652. Hence the visible radiations of the mercury arc and a glass spectrograph had to be used, and the recording of the complete Raman spectrum was found to be far from easy, since in the first place the crystals were of rather small size and not completely free from flaws and since they also exhibited a faint luminescence. A strong and sharp line at a shift of 332 cm.$^{-1}$ and a strong but slightly diffuse line at 1096 cm.$^{-1}$ with a width of about ten wave-numbers were the principal features recorded on all the plates. By interposing a filter of $NaNO_2$ solution to suppress λ 4046 from the incident radiation and by placing a thin opaque strip just before the photographic plate to screen the exciting radiation λ 4358, clearer spectra were recorded in which could be observed and measured a line with a frequency shift of 212 cm.$^{-1}$ In some particularly clear spectrograms, a weak and rather diffuse line was found with a frequency shift of 735 cm.$^{-1}$ By analogy with the Raman effect in calcite one should expect one more line with a frequency shift in the vicinity of 1450 cm.$^{-1}$ A faint trace of such a line was found on one of the plates with an estimated frequency shift of 1460 cm.$^{-1}$

2. Discussion of Results

Magnesite has the same crystal structure as calcite belonging to the space-group D^6_{3d} of the trigonal system. Dolomite has also a similar structure, though it belongs to the space-group C^2_{3i}. In view of the similarity of crystal structure and chemical composition it is of interest to compare their Raman spectra. Table I shows the observed frequency shifts and their relative intensities in the case of calcite, dolomite and magnesite. The data for calcite are from a paper by Krishnan[3] while those for dolomite are due to Couture[4] by whom the Raman effect in dolomite has been investigated in detail.

Table I

Raman Frequencies

Substance	Frequency shifts in cm.$^{-1}$					
$CaCO_3$.	156 (8)	284 (15)		712 (2)	1086 (20)	1434 (5)
$CaMg(CO_3)_2$	176 (9)	301 (10)	335 (0·3)	724 (2)	1099 (23)	1444 (1·4)
$MgCO_3$ . .	212 (w)	332 (st)		735 (w)	1096 (st)	1460 (?)

As is to be expected, Table I exhibits a close similarity between the Raman spectra of calcite, dolomite and magnesite. All the frequencies of magnesite are definitely higher than those observed with calcite, this feature being more pronounced for the lattice oscillations than for the internal frequencies of the CO_3 group. An explanation of this feature is to be sought for in the fact that the lattice constants of calcite and magnesite are respectively 6·36 A.U., and 5·61 A.U., indicating a notable decrease in the interionic distances in the latter case. This would result in an increase of the interionic forces and hence also of the vibration frequencies involving the CO_3 groups.

Schæfer *et al.*[5] have studied the infra-red reflection and absorption spectra of magnesite and observed the following frequencies amongst others: Reflection Spectrum: 726, 889 and 1495 cm.$^{-1}$; Absorption Spectrum: 730, 877, 899 and 1430 cm.$^{-1}$ The only study on the far infra-red reflection spectrum of magnesite was by Coblentz[6] who observed a reflection maximum at 30·7 μ, *i.e.*, 326 cm.$^{-1}$ It will be noticed from the data that the frequency observed at 889 cm.$^{-1}$ in the infra-red does not appear in the Raman effect, whereas the frequency 1096 cm.$^{-1}$ observed in the Raman effect does not

appear in infra-red absorption. These facts are in accordance with the theoretical analysis of the vibrations of the calcite structure by Bhagavantam and Venkatarayudu.[7]

The author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for suggesting this investigation and for the kind interest he took in it.

SUMMARY

The Raman spectrum of magnesite ($MgCO_3$) has been investigated and found to be analogous in its features to that of calcite, as is to be expected in view of the similarity of structure. The frequency shifts observed are: 212 (*w*), 332 (*st*), 735 (*w*), 1096 (*st*) and 1460 (?) cm.$^{-1}$ All the frequencies and especially the two lowest are notably higher than for calcite and this is explicable as due to the smaller interionic distances and correspondingly larger force constants.

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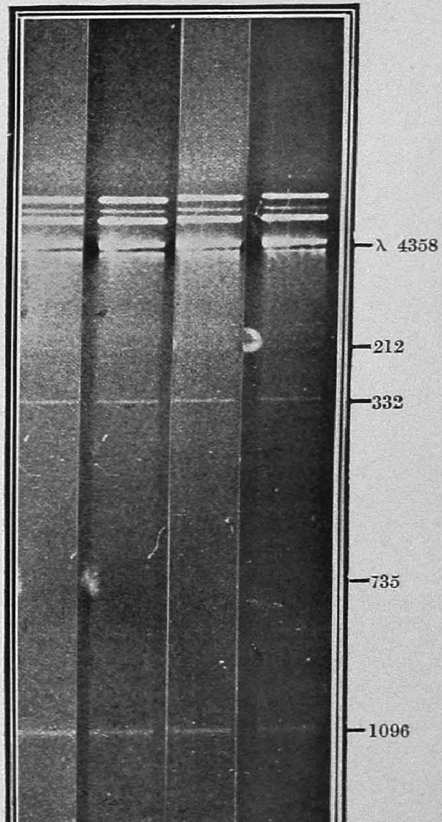


Raman Spectrum of Magnesite

Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XLIII, No. 6, Sec. A, 1956

THE PHYSICS OF CRYSTALS*

BY SIR C. V. RAMAN
(*Memoir No. 85 of the Raman Research Institute, Bangalore 6*)

Received May 31, 1956

1. INTRODUCTION

IT is the aim of this address to give a fresh orientation to the subject of crystal physics. We begin with a re-examination of the fundamental notions on which a theoretical approach to the problems of the subject has to be based. The ideas which emerge are then applied to find an answer to the following questions: What is the nature of the thermal agitation in crystals? What is the character of their vibration spectra? These questions are of fundamental importance since they confront us in any attempt to explain or interpret the physical behaviour of crystals. The results which emerge from our enquiry impinge on many aspects of crystal physics. But we shall restrict ourselves here to a consideration of those in which the relationships between theoretical reasoning and factual experience are most evident, *viz.*, the thermal properties of crystals and their spectroscopic behaviour. Even in these fields, we can here do no more than broadly indicate the general nature of the results which follow from the application of the new ideas.

2. THE THEORY OF EINSTEIN

It is appropriate that we begin with a reference to the classic paper of 1907 by Einstein introducing the quantum theory of specific heats, a paper which even fifty years after its publication remains worthy of careful study. Einstein commences his paper by showing that the acceptance of Planck's radiation formula demands as a necessary consequence that the energy of a resonator capable of absorbing or emitting radiation with a specific frequency can only increase or diminish by quanta proportional to that frequency. *It is inferred that the energy of any elementary structure capable of mechanical vibration should likewise obey the quantum rule.* Einstein then indicates a procedure which enables this principle to be applied to the case of crystals. He identifies the thermal energy of a crystal with the mechanical energy of vibration of an immense number of *individual* oscillators distributed over its volume, the total number of these oscillators being the same as thrice the number of atoms comprised in the crystal. It is assumed that

* Address to a Conference of Nobel Laureates at Lindau on the Lake of Constance, June 25th to 29th, 1956.

the oscillators could be grouped into sets; each set comprises a great number of individual oscillators characterised by a common frequency of vibration. The individual oscillators in each set occupy the various energy levels allowed by the quantum hypothesis for the particular frequency. The numbers occupying these levels are in the relative proportions determined by the respective energies and by the temperature as indicated by the principle of Boltzmann. The average energy of an oscillator in each of the sets is then evaluated. Summing up over all the oscillators in each of the sets, and then over all the sets, Einstein obtains an explicit formula for the thermal energy of the crystal as a function of the temperature.

Examining the procedure thus summarised, it is evident that every step in the argument can be justified. A crystal is an assembly of a great number of similar and similarly situated groups of atoms, the normal modes and frequencies of vibration of which would necessarily all be identical. The total number of degrees of dynamical freedom of the entire system may accordingly be divided up into sets, each set representing a great number of individual oscillators having a common frequency. Since these oscillators are interconnected, they can exchange energy with each other and thereby constitute a system in thermodynamic equilibrium of which the behaviour could be statistically described in terms of Boltzmann's principle. In other words, the procedure followed effects a synthesis of the results of classical dynamics with the notions of the quantum theory and the basic principles of thermodynamics. The simplicity of Einstein's theory is as noteworthy as its success in explaining the general character of the specific heat-temperature curve of crystals.

We conclude, therefore, that Einstein's approach to the problem is fundamentally correct. His theory indicates that the atomic vibration spectrum of a crystal would consist of a set of discrete monochromatic frequencies, their number being the same as the number of sets of oscillators which are the carriers of the thermal energy. By virtue of Boltzmann's principle, the distribution of this energy over the volume of the crystal would exhibit fluctuations both in space and in time, the magnitude of the fluctuations being the greater the higher the frequency of the oscillators under consideration. However, the theory as it stands gives no precise indication of how the oscillators in each set are to be enumerated and how their respective frequencies of vibration are to be determined. Neither is any indication given whether the modes of vibration of the solid recognised by the classical theory of elasticity have any place in the picture. We shall now proceed to show how these lacunæ in Einstein's theory may be filled up.

3. The Dynamics of Crystal Lattices

The fundamental role which the enumeration of the degrees of freedom of atomic movement plays in specific-heat theory derives its justification from the well-known theorem in classical mechanics regarding the small vibrations of a connected system of particles about their positions of equilibrium. This theorem states that all the possible oscillations of the system are superpositions of its normal modes of vibration in each of which all the particles of the system vibrate with the same frequency and in the same or opposite phases. On the other hand, in Einstein's theory we are concerned with the modes and frequencies of vibration of the *individual* oscillators of which the total number is equal to the number of degrees of dynamical freedom of the entire system. These two points of view can be reconciled by identifying the normal modes and frequencies of vibration which are characteristic of the structure of the crystal with those that describe the dynamical behaviour of the elementary units of which it is composed.

The fundamental property of crystal structure is that it comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. Hence, the normal modes of vibration characteristic of the structure of a crystal should satisfy a similar requirement. This can evidently happen in two ways, *viz.*, the amplitudes and phases of oscillation of equivalent atoms in adjacent cells are the same; alternatively, the amplitudes are the same while the phases are all reversed following the unit translation. Since these two possibilities exist for each of the three axes of the lattice, we have $2 \times 2 \times 2$ or eight possible situations. In each of these situations, the equations of motion of the p atoms contained in the unit cell can be completely solved, yielding us $3p$ solutions. Thus in all, we have $24p$ solutions from which the three simple translations must be excluded. We are then left with $(24p-3)$ normal modes and frequencies of vibration. Thus, the fundamental result emerges that a crystal consisting of p interpenetrating Bravais lattices of atoms has $(24p-3)$ characteristic modes of vibration, each of which is characterised by a specific frequency. In $(3p-3)$ of these modes, equivalent atoms have the same amplitudes and phases of oscillation in the adjacent cells, while in the $21p$ other modes the amplitudes are the same, while the phases alternate in adjacent cells along one, two or all three of the axes of the lattice.

The $(24p-3)$ normal modes of vibration indicated by the preceding argument may obviously be regarded as the modes of internal vibration of the group of $8p$ atoms comprised in a supercell of the crystal lattice whose linear dimensions are twice as large as that of the unit cell containing p

atoms. The 3 omitted degrees of freedom would then represent the 3 degrees of translatory freedom of movement of the whole group of 8 p atoms included in the supercell. Thus, it emerges that the structural unit whose dynamical behaviour is representative of the entire crystal is not the unit cell of the crystal structure but is twice as large in each direction as the latter.

4. THE VIBRATION SPECTRUM OF A CRYSTAL

The considerations set forth above indicate that a crystal may be regarded as an assembly consisting of $(24\,p\text{–}3)$ sets of similar oscillators, each with its own distinctive vibrational frequency. Even a monatomic crystal for which $p = 1$ would have 21 characteristic frequencies, while a diatomic crystal for which $p = 2$ would have 45 and so forth. The number of distinct frequencies would however be reduced considerably if the crystal belongs to a class with a high degree of symmetry. For instance, it can be readily shown that a face-centred cubic lattice of atoms would have only four characteristic frequencies of vibration, while cubic crystals such as diamond and rock-salt having two non-equivalent atoms in the unit cell would each have nine distinctive frequencies. The important point to be emphasised is that the vibration spectrum of a crystal consists of a set of discrete monochromatic frequencies whose number is the greater, the more numerous the atoms included in its unit cell are or the lower the symmetry of the crystal.

To complete the picture, we have to consider the nature of the movements associated with the three omitted degrees of freedom representing the translatory movements of the supercell of the crystal lattice. Such translations would necessarily result in local stresses and strains of the same general nature as those contemplated in the theory of elasticity and hence would also give rise to localised oscillatory movements. In other words, to complete the picture of the thermal agitation envisaged in Einstein's theory, we have to superpose on the oscillations of precisely defined frequencies determined by the atomic structure of the crystal, other quantized oscillations whose frequencies are not so precisely defined, since they would depend upon the dimensions of the moving masses and the forces thereby brought into play. It is evident that the smaller the mass of the oscillators under consideration, the more numerous they would be and also the higher their frequencies of vibration. It follows that the spectrum of the thermal agitation represented by such movements would be continuous and would exhibit a concentration of frequencies most marked at the upper end of the frequency range and falling off rapidly to zero as we move towards the lower end of the range.

5. The Theories of Debye and Born

The views set forth above regarding the nature of the thermal agitation in crystals and the character of their atomic vibration spectra are essentially a justification and a development of the original ideas of Einstein outlined in his fundamental paper of 1907. It is a matter of scientific history, however, that an approach of an entirely different nature to the problems of crystal physics was put forward a few years later and found general acceptance. The reference here is to Debye's theory of specific heats familiar to all students of physics and chemistry and to the lattice dynamics of Born and his collaborators which is regarded with favour by the mathematical theorists. The theories of Debye and Born differ in detail, but the basic idea in both is the same, namely that we are here dealing with a boundary value problem in the theory of wave-propagation. Actually, what we are concerned with is the determination of the modes and frequencies of vibration of the atoms in a crystal about their positions of equilibrium. These modes and frequencies would be determined by the masses of the atoms and their interactions with the surrounding atoms in a domain the extent of which is limited by the range of the interatomic forces. It follows that considerations regarding wave-propagation and boundary conditions are not relevant to the problem.

A rigorous mathematical investigation of the theory of the propagation of waves in a general crystal consisting of p interpenetrating lattices of atoms on the basis of the classical mechanics shows that only in the limiting cases of the lowest frequencies of vibration is the group velocity of the waves identifiable with their phase velocity. With increasing frequency, the phase velocity and the group velocity diverge from each other, and the group velocity becomes zero for $(24p-3)$ distinct frequencies, the nature of the atomic modes of vibration for these frequencies being identical to the $(24p-3)$ normal modes of vibration of the structure of the crystal referred to earlier in this address. Thus, the investigation from the standpoint of the theory of wave-propagation and of classical mechanics leads to the same result, namely that these are the $(24p-3)$ characteristic modes and frequencies of vibration of the structural units of which the crystal is composed.

We may put the matter a little differently by saying that while Einstein's theory identifies the thermal energy of a crystal with the quantized vibrational energy of immense numbers of oscillators having identical frequencies, Born's lattice dynamics identifies it with the quantized energy of immense numbers of wave-motions whose frequencies are all different. The two approaches are clearly irreconcilable, since in the one case, the vibration spectrum of

the crystal consists of a set of discrete frequencies, while in the other, it is a continuous spectrum. That Born's approach to the specific heat problem is indefensible becomes evident when we remark that his " waves " are not normal modes and hence are incapable of enumeration.

6. THE THERMAL PROPERTIES OF CRYSTALS

We shall now consider the application of the ideas indicated in the present address to the interpretation of the physical behaviour of crystals. The thermal properties may be considered first, since the nature of the thermal agitation plays a leading role in relation to them.

A familiar fact of experience is the extreme slowness with which heat diffuses through a solid. On the other hand, elastic waves travel through a solid with a velocity of some thousands of metres per second. It would be a formidable problem to explain such a fundamental difference in behaviour, if one were to identify thermal energy with wave-motion, as is done in the theories of Debye and Born. Such a paradox does not however confront us on the present view of the nature of the thermal agitation in which it is identified with the energy of vibration of individual oscillators localised in the crystal. The conduction of heat through a solid would on this view be the result of an exchange of energy quanta between the individual oscillators. Such a process would bear no resemblance whatever to wave-propagation in the ordinary sense of the word.

The evaluation of the specific heats of crystals as a function of temperature reduces itself to the problem of determining the $(24p-3)$ characteristic frequencies of atomic vibration. When p is unity or a small integer, the $21p$ superlattice frequencies make important contributions to the thermal energy. When p is large, however, the $(3p-3)$ modes and frequencies of the unit cell reappear with only minor changes as superlattice modes and frequencies, and hence many of the latter could be identified with the former without sensible error in the calculation of the thermal energy; a considerable simplification thereby results. The thermal energy represented by the three translations of the supercell may be assumed to be proportional to the absolute temperature, except at the very lowest temperatures where its continuous spectrum of frequencies would have to be explicitly to be taken into consideration.

Crystals exhibit a surprising variety of behaviour in respect of the changes in their linear dimensions with rise or fall of temperature. The present view of the nature of thermal agitation which regards it as a localised vibration of individual oscillators opens a pathway to the interpretation of

the observed facts. The finite amplitudes of vibration of the individual oscillators and the mechanical anharmonicity associated therewith would result in the frequencies of vibration diminishing in the higher states of excitation. It would also result in a change of the average dimensions of the individual oscillators, which again would depend on the modes of vibration and hence may be very different in different directions. The integrated effect would be a shifting accompanied by a broadening of the lines in the vibration spectra and a change in the linear dimensions of the crystal. Thus, a close correlation is to be expected between the thermal expansion of crystals and the changes in their spectroscopic behaviour with rise or fall of temperature.

7. The Spectroscopic Behaviour of Crystals

The vibration spectra of crystals are accessible to experimental study with a great variety of materials and by diverse techniques of investigation. The nature of the spectra becomes manifest when the absorption of light by crystals exhibiting visible colour (*e.g.*, the inorganic chromates), or of ultra-violet light by crystals (*e.g.*, the aromatic organic compounds) is investigated with the crystals cooled down to the lowest possible temperatures. The absorption spectra then appear fully resolved into a set of sharply defined lines. These can be interpreted as combinations of the electronic with the vibrational frequencies of the crystal. Very low temperatures are also necessary for effecting a similar resolution into sharp lines of the luminescence spectra of various crystals of which such luminescence is an inherent property, *e.g.*, the uranyl salts and of other crystals of which the luminescence is ascribable to the presence of an impurity phosphor (*e.g.*, ruby). Such luminescent crystals also exhibit at low temperatures characteristic absorption spectra which are resolved into discrete lines and which are related by an approximate mirror image symmetry to their emission spectra.

There are also other and rather more direct methods of investigation. Three different techniques based on infra-red spectroscopy are available, *viz.*, the emission, absorption and reflection of infra-red radiations by crystals. In these techniques, the disturbing effects of thermal agitation and of the anharmonicity of the vibrating electric doublets in the crystal are strongly manifested. Nevertheless, by an appropriate choice of the material to be investigated and of the techniques used, *e.g.*, by varying the thickness of the crystal, cooling it to low temperatures and the application of adequate resolving power, it is possible to obtain results capable of unequivocal interpretation. Finally, we have the method based on the study of the scattering

of light in crystals. The results obtained by this method are of such importance that they will be considered separately in the next section.

The whole body of experimental evidence forthcoming with the materials and methods described above confirms the thesis that apart from disturbing effects such as those mentioned earlier, the atomic vibrations in crystals appear as a set of sharply defined monochromatic frequencies in the spectrum.

8. THE SCATTERING OF LIGHT IN CRYSTALS

The nature of the results to be expected when a crystal is traversed by an intense monochromatic beam of light is different in relation to the $(3p-3)$ modes of atomic vibration which have the same phase in adjoining cells of the lattice, and the $21p$ modes in which the phases are opposite in adjoining cells along one, two or all three of the axes of the lattice. In either case, we are concerned with the scattered radiations having their origin in the changes of optical polarisability of the vibrating atomic groups. Ordinarily, except in the cases where the symmetry of the vibrational modes results in there being no resultant change of optical polarisability, the $(3p-3)$ modes would manifest themselves as frequency shifts in the spectrum of the scattered light. On the other hand in the $21p$ modes, the optical moments being in opposite phases in adjoining cells, their effects would cancel out. However, if the amplitudes of vibration are sufficient, the changes in optical polarisability proportional to the squares of the atomic displacements would also have to be considered. It is then possible for all of the $(24p-3)$ modes of atomic vibration to appear with doubled frequency shifts in the spectrum of the scattered light. The intensity of such scattering, being proportional to the square of the absolute atomic displacements, would necessarily be small. Strongly exposed spectrograms would accordingly be necessary to record the same.

It is evident that the study of the second-order spectra of light-scattering is of the greatest importance, since in the first place they allow us to observe and measure the frequencies of modes which do not appear in the first-order spectrum, and secondly because the intensity of the lines of the second-order spectra relative to those of the first-order spectra is a measure of the absolute magnitude of the interatomic displacements responsible for the changes in optical polarisability. Studies of this kind are obviously most suitably undertaken with crystals of relatively simple structures, as for example, diamond, rock-salt, calcite and quartz, since the results are then most readily interpreted.

Very detailed investigations of the kind indicated carried out at Bangalore have established that the vibration spectra of crystals include both the $(3p-3)$ and the $21p$ modes with discrete monochromatic frequencies, and further that the oscillators whose vibrations manifest themselves as frequency shifts are of the same order of magnitude in their dimensions as the unit cells of the crystal structure. The latter result is inferrable from the fact that the relative intensity of the first- and the second-order spectra is of the same order of magnitude in crystals as in fluids. For, the size of the quantized oscillators emitting the scattered radiation of any given frequency determines the absolute magnitude of the interatomic displacements responsible for the variations of optical polarisability.

Summary

1. Einstein's view of a crystal as an assembly of immense numbers of quantized oscillators having a common set of vibration frequencies is not only the logical and correct view of the matter but also proves itself when fully developed to be an eminently successful view. It gives us a deep and quantitative insight into the thermal behaviour of solids. The nature of the vibration spectra of crystals indicated by it is confirmed in detail by the results of spectroscopic studies with diverse materials and by various techniques and with especial completeness by studies on the diffusion of light in crystals.

2. The ideas underlying the specific-heat theories of Debye and Born are irreconcilable with the observed spectroscopic behaviour of crystals and especially with the effects exhibited in their second-order spectra of light-scattering.

Reprinted from "The Proceedings of the Indian Academy of Sciences", Vol. XLIV, No. 3, Sec. A, 1956

THE DIAMOND*

By Sir C. V. Raman

(*Memoir No. 86 from the Raman Research Institute, Bangalore-6*)

Received September 5, 1956

1. Introduction

The many remarkable properties which diamond exhibits, taken in conjunction with the simplicity of its crystal structure and composition, make it a substance of quite exceptional interest to the physicist. In the hope that investigations made with it would result in significant contributions to knowledge, a collection of some five hundred diamonds was built up in the course of years and used by the present author and his collaborators in an extensive series of researches. It would not be possible in this lecture to survey all the topics investigated. We shall confine ourselves to the consideration of some results which have emerged from our studies and which are of fundamental significance for the physics of the solid state.

In his paper of 1907 introducing the quantum theory of specific heats, Einstein made use of the experimental data for the variation with temperature of the specific heat of diamond which had been discovered by earlier investigators to demonstrate the correctness of the basic ideas set out in his paper. The expression for the thermal energy of crystals as a function of temperature derived by Einstein in that paper was a logical deduction from his hypothesis that the structural units comprised in the crystal and capable of mechanical vibration obey the quantum rule, in other words, that their energy can only increase or diminish by quanta proportional to the frequency of vibration. Einstein did not however, deal with the question of how the modes and frequencies of vibration under consideration could be evaluated in the general case. In my address to the Lindau Conference this year, I showed how this basic problem can be handled rigorously and a solution obtained which reconciles the results of classical dynamics with the fundamental notions of the quantum theory and the principles of thermodynamics. Diamond is exceptionally well-suited for a test of the correctness of the theoretical approach set out in that address, since the necessary calculations are readily made and the experiments necessary to check the consequences of the theory are also feasible. It is the purpose of this lecture to show how perfectly the

* A lecture delivered at the Federal Polytechnic Institute in Zurich and at the Universities of Freiburg and Bonn early in July 1956, following the address on "The Physics of Crystals" given at Lindau in June, 1956. The latter address has been published in these *Proceedings* (Memoir No. 85 of the Institute), but the present memoir may be read independently of the same.

theory and the results of experiment are in accord with each other. For the sake of ready intelligibility, the subject will be dealt with from first principles.

2. THE CHARACTERISTIC VIBRATIONS OF LINEAR LATTICES

We shall commence by considering a few simple models of which the behaviour may serve to illustrate the principles underlying the general theory. The simplest of such models is a stretched string loaded by a series of equidistant particles of identical mass along its length. It is immediately obvious that a mode of oscillation is possible on such a string in which the successive particles have the same amplitude but opposite phases of vibration. Such an oscillation is pictured in Fig. 1 (*a*). It has all the characters of a normal mode of vibration and possesses a specific frequency which can therefore be regarded as characteristic of the system. We may next consider the case in which the particles on the string are equidistant but have alternately two different masses. It can be seen that such a system would have *three* possible modes of normal vibration with different frequencies. These modes are represented in Fig. 1 (*b*), (*c*) and (*d*) respectively. In Fig. 1 (*b*), successive particles of equal mass have identical amplitudes and oscillate in the same phase, while in Figs. 1 (*c*) and 1 (*d*), they have the same amplitudes but opposite phases, the situation thus being analogous to that pictured in Fig. 1 (*a*).

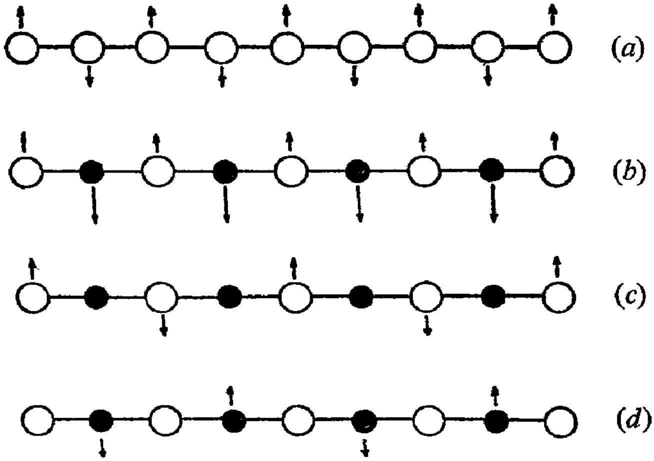


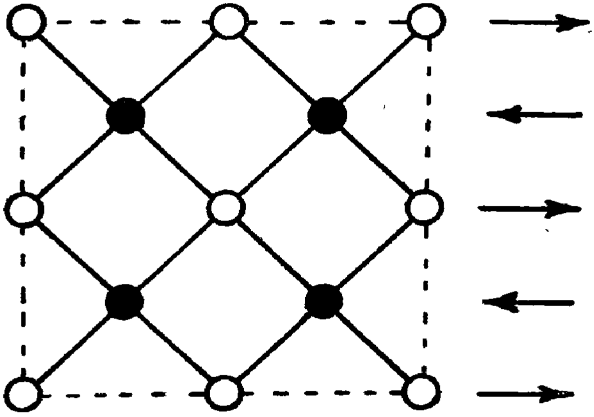
FIG. 1. The characteristic vibrations of linear lattices.

The foregoing results can readily be generalized. It can be proved that a periodic linear lattice with p particles in each unit of its structure would have $(2p-1)$ normal modes and frequencies of vibration; in $(p-1)$ of these

modes, the amplitudes and phases of vibration of the corresponding particles in the successive units are the same, while in the p other modes, they have the same amplitudes but opposite phases. It can also be shown analytically that any initial disturbance set up locally on such a linear lattice would resolve itself quickly into a summation of the $(2p-1)$ characteristic modes of oscillation with their respective frequencies.

3. The Normal Vibrations of Crystal Structures

The basic principle of crystal architecture is that its structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. It follows as a necessary consequence that the normal modes of vibration of the atoms characteristic of the structure of the crystal should possess the same property. This can evidently happen in two ways, thereby enabling us to divide the normal modes in two distinct classes. In the first class of normal modes, the amplitudes as well as the phases of oscillation of the equivalent atoms which come into coincidence following an unit translation are identical. In the second class of normal modes, the amplitudes of equivalent atoms are the same but the phases are all reversed. Since these two alternatives are possible for a unit translation



Mode I.

Fig 2. Diamond: the principal mode of oscillation.

along each of the three axes of the lattice, we have $2 \times 2 \times 2$ or 8 possible situations. In each of these situations, the equations of motion of the p atoms contained in the unit cell of the structure can be written down and completely solved, giving us $3p$ solutions. Thus in all we have $24p$ solutions. $(3p-3)$ of these solutions represent normal modes of vibration of the first kind, $21p$ solutions represent normal modes of the second kind and the 3

remaining solutions represent the simple translations of the unit cell of the structure.

The general principles set forth above enable us to describe in simple geometric terms, the normal modes of vibration of the atoms located at the points of a Bravais lattice for each of the known fourteen species. In the general case when $p = 1$, we have 21 distinct normal modes and frequencies of vibration, besides the three translations. But, if the lattice possesses some elements of symmetry, the number of distinct frequencies would be notably reduced. We shall consider here the case of the face-centred cubic lattice. The primitive translations in such a lattice may be taken as the lines joining a cube corner with the centres of the three cube faces meeting at that corner. Applying the symmetry operations of the point group O_h to which the lattice belongs and considering the 8 possible combinations of the phases of atomic vibration, the 21 modes of vibration which thereby result can be grouped together and described as follows: I: a vibration of the alternate octahedral planes of atoms with opposite phases normally to themselves (degeneracy 4); II: the same but transversely to the planes (degeneracy 8); III: the vibrations of the cubic planes of atoms normally to themselves (degeneracy 3); IV: the same but with the vibrations tangentially to the planes (degeneracy 6). The same results can be very simply deduced by inspection of a model exhibiting the unit rhombohedral cells in a face-centred cubic lattice.

4. THE VIBRATIONS OF THE DIAMOND STRUCTURE

The structure of diamond may be described as an interpenetration of two face-centred cubic lattices of carbon atoms, each atom in one lattice being linked to its four nearest neighbours in the other lattice by tetrahedrally directed valence bonds. This situation is diagrammatically represented in Fig. 2 by a projection of the cubic cell on a plane normal to the cubic axis. (No attempt is made to show the different planes in which the atoms lie.)

The normal modes of vibration of the atoms in the diamond structure may be very simply derived from those for a simple face-centred lattice listed above by taking into account the phases of the motion of the atoms in the two lattices which may be either the same or opposite. The nine possible modes of vibration thus derived are depicted in Figs. 2, 3 and 4. The principal mode which is depicted in Fig. 2 is a translatory movement of the two lattices in opposite phases. This is triply degenerate and can occur along anyone of the three cubic axes, as indicated by the arrows in the figure. Fig. 3 shows the diamond structure viewed in a direction normal to a trigonal axis of symmetry and exhibits the octahedral layers of atoms. The normal and tangential movements of these planes in the two possible relative phases

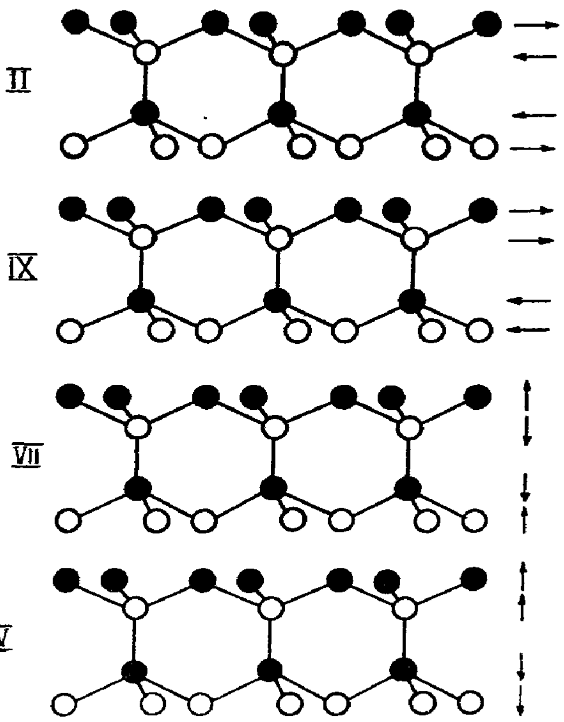


FIG. 3. Diamond: normal and tangential oscillations of the octahedral layers.

give us four modes of vibration; the directions of movement of the atomic planes are indicated by arrows in the figures. Fig. 4 shows the structure of diamond as viewed in a direction slightly inclined to a face diagonal and exhibits the cubic layers of atoms. The directions of movement of these layers in the four possible modes are likewise indicated by arrows in the figure.

Very simple considerations enable us to arrange the nine normal modes of vibration of the diamond structure in the descending order of their frequencies as indicated by the Roman numerals entered against them in Figs. 2, 3 and 4. The triply degenerate oscillation of the two interpenetrating lattices against each other shown in Fig. 2 would evidently have the highest frequency of all, since the movement involves variation of all the four bond lengths and all the six bond angles at each carbon atom; the restoring forces brought into play would therefore be the maximum possible. It is likewise evident that the mode marked IX in Fig. 3 would have the lowest frequency of all and the mode marked VIII in Fig. 4 would be the next lowest. For, in neither of these modes is there any variation of the bond lengths; in mode

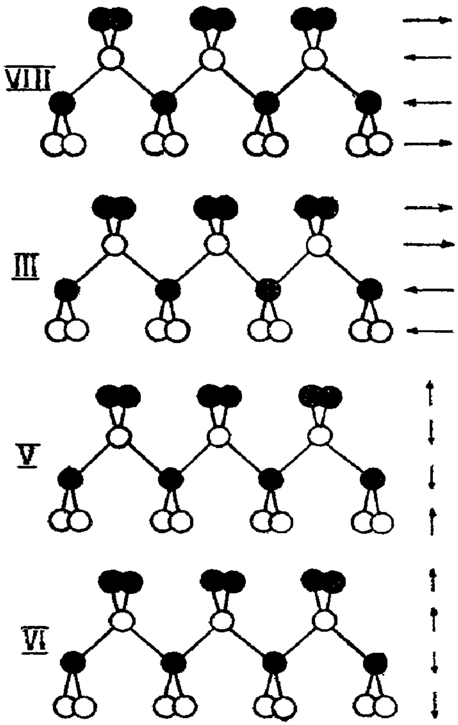


FIG. 4. Diamond: normal and tangential oscillations of the cubic layers.

IX, only two bond angles vary and in mode VII only four bond angles, the rest of them remaining unaltered. *Per contra*, the same modes but with the relative phases of motion of the adjacent layers reversed, *viz.*, mode II shown in Fig. 3 and mode III shown in Fig. 4 may be expected to have high frequencies which follow that of mode I in the order indicated. It remains to determine the sequence of the frequencies of the four remaining modes. It is obvious that the modes marked V and VI in Fig. 4 would have identical frequencies; for in these modes, the cubic layers which move normally to themselves, in other words along the cubic axis, are equidistant. Finally, we remark that the modes marked IV and VII in Fig. 3 may be expected to have frequencies respectively higher and lower than the common frequency of modes V and VI, though the differences would not be large. In mode IV, the oscillation involves the maximum stretching of one bond out of the four in the successive layers of the structure, the three others remaining invariable, while the mode VII, the bond along which the motion takes place remains of invariable length, while the three other bonds inclined at a large angle to the direction of movement are tilted periodically. The restoring forces

acting in the direction of movement may be expected to be distinctly greater in the former case than in the latter.

5. Numerical Evaluation of the Frequencies

Exact formulæ are readily derived for the eight distinct frequencies of vibration in terms of the force constants expressing the interactions between each carbon atom and the surrounding ones. The equations of motion from which these formulæ are derived take a very simple form by reason of the fact that the relative displacements of the atoms are either zero or else are twice the value of the absolute displacement of each atom. The force-constants are most conveniently defined in terms of the components of the relative displacements and the forces of interaction resolved along the three cubic axes and considering their ratios. The symmetry of the structure results in a very considerable diminution in the number of distinct force-constants: it is found that two constants express the interactions with the four nearest neighbours, five others the interactions with the twelve next nearest neighbours, and five more the interactions with the twelve more distant neighbours. However, on writing down the equations of motion, it emerges that only three of the five force-constants for the next nearest neighbours actually appear in them and that the five force-constants for the twelve more distant neighbours also appear in the equations as sums of which there are only two. Accordingly, if we restrict ourselves to the interactions with the twenty-eight nearest neighbours of any given atom, we have only seven force-constants to deal with.

The seven force-constants referrred to above will be denoted by α, β for the first four atoms; θ, ϕ, ψ for the next twelve and k and χ for the twelve atoms still further out. By way of explanation, it may be stated that the force-constant α refers to the case in which the force and displacement are both along the same cubic axis, while β refers to the case in which they are mutually perpendicular. The constant θ refers to the case in which the force and displacement are parallel to each other but are both perpendicular to the line joining the atoms which is a face-diagonal of the cube; ϕ and ψ refers to the cases in which the component forces and displacements both lie in the same plane as this diagonal, but the force and displacement are parallel to each other for ϕ and perpendicular for ψ. The constant k refers to the cases in which the components of force and displacement are parallel to each other while χ refers to the cases in which they are mutually perpendicular. k and χ both represent the joint effect of a whole set of twelve atoms.

Table I shows the eight frequencies of vibration arranged in the sequence already explained which will be found entered in the first column. The

TABLE I

Evaluation of Frequencies

Mode No.	Degeneracy	Complete formula $4\pi^2\nu^2c^2m =$	α, β only	α, β, θ, ϕ, ψ only	α, β, θ, ϕ, ψ, k, χ
I	3	$4\alpha + 12k$	1332	1332	1332
II	8	$3\alpha+\beta+2\theta+4\phi-2\psi+3k-3\chi$	1250	1285	1250
III	6	$2\alpha+2\beta+4\theta+4\phi+6k+6\chi$	1162	1232	1239
IV	4	$\alpha+2\beta+2\theta+4\phi+4\psi+9k-6\chi$	952	1099	1149
V & VI	3+3	$2\alpha+8\phi+6k$	942	1088	1088
VII	4	$3\alpha-2\beta+2\theta+4\phi+4\psi+3k+6\chi$	931	1068	1008
VIII	6	$2\alpha-2\beta+4\theta+4\phi+6k-6\chi$	651	752	740
IX	8	$\alpha-\beta+2\theta+4\phi-2\psi+9k+3\chi$	460	538	621

second column shows the degeneracy of each of these modes. The total of the figures shown in this column amounts to forty-five as is to be expected. The third column shows the operative force-constants in each case in terms of the seven force-constants, *viz.*, α, β for the first group; θ, ϕ, ψ for the second group; k and χ for the third group. In the fourth, fifth and sixth columns are given respectively the values of the frequencies calculated with only the first two constants, then with only five and finally with all the seven. The values of the constants in each case have been so chosen as to give the same frequency for the principal mode. They are given in Table II.

It will be remarked from Tables I and II that even with only two force-constants we obtain a rough approximation to all the frequencies and that with five constants we get a fair approximation to the values calculated with all seven constants shown in the last column of Table I. It will also be seen from Table II that the force-constants fall off rapidly in magnitude as we proceed to the more distant neighbours. The magnitudes of the force-constants in each group are also related to each other in the manner that could have been expected *a priori* from their respective definitions as given above.

TABLE II

Values of Force-Constants Used

Force-constants	Table I, Column 4	Table I, Column 5	Table I, Column 6
α	$3\cdot135\times10^5$ dynes/cm.	$3\cdot135\times10^5$ dynes/cm.	$2\cdot78\ \times 10^5$ dynes/cm.
β	$1\cdot637\times$,,	$1\cdot682\times$,,	$1\cdot746\times$,,
θ	..	$0\cdot012\times$,,	$0\cdot010\times$,,
ϕ	..	$0\cdot262\times$,,	$0\cdot262\times$,,
ψ	..	$0\cdot240\times$,,	$0\cdot228\times$,,
k	..	..	$0\cdot12\ \times$,,
χ	..	..	$0\cdot00\ \times$,,

6. THE SCATTERING OF LIGHT IN DIAMOND

Spectrograms of the light scattered by diamond when illuminated by the light of a mercury arc lamp exhibit, for each of the monochromatic radiations of the incident light, a single sharp line with a frequency shift of 1332 cm.$^{-1}$ which may be identified with the highest of the frequencies listed in Table I. But no lines appear with frequency shifts other than that mentioned. This is readily understood, since in all the modes except that of the highest frequency, the atomic oscillations have opposite phases in the successive layers, and hence the effects arising at these layers cancel each other out. Overtones and combinations of the frequencies of all the normal modes are, however, permitted to appear as frequency shifts in light scattering, thereby making the existence of these modes open to observation. That diamond would exhibit this type of light-scattering was theoretically predicted, following which experimental studies undertaken by Dr. R. S. Krishnan confirmed the expectations.

The second-order spectrum of light scattering is of extremely low intensity, and one has necessarily to use diamonds of small size for the experiments. Further, it is necessary to record the spectrum under high dispersion to enable its features to be adequately exhibited. These difficulties are successfully overcome by the aid of the extremely intense λ 2537 radiations

emitted by a quartz water-cooled mercury arc when it is set between the poles of an electro-magnet. It is necessary, of course, to employ diamonds which are transparent to the ultra-violet region of the spectrum. In these circumstances, it is also essential to use mercury vapour as a filter inside the spectrograph to absorb the intense λ 2537 radiations before they reach the photographic plate, and thus prevent its fogging.

Spectrograms obtained in the manner explained are reproduced as Fig. 1 in Plates II and III respectively. The spectrum in Plate II was recorded with a medium-sized spectrograph and that in Plate III with a larger instrument of higher resolving power. A microphotometer record of the spectrum obtained with the smaller instrument is reproduced in juxtaposition with the spectrum itself as Fig. 2 in Plate II, below which has been placed the spectrum of the mercury arc alone as a comparison. Fig. 2 in Plate III reproduces the microphotometer record of the second-order spectrum obtained with the larger instrument and below it the spectrum itself to admit of ready comparison with the features seen in it.

The features visually observed in the spectra and confirmed by inspection of their microphotometric records are diagrammatically represented in Fig. 5 below, the measured frequency shift being indicated against each feature.

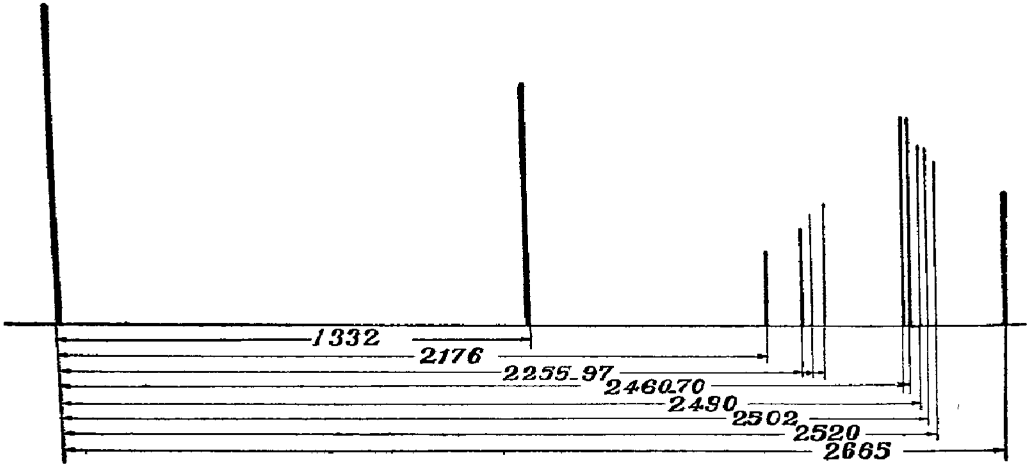


FIG. 5. Frequency shifts in light scattering.

Very conspicuous is the sharply defined peak of intensity terminating the s cond-order spectrum and exhibiting a frequency shift of 2665 cm.$^{-1}$ This is clearly to be identified as the octave of the principal mode of vibration having a frequency shift of 1332 cm.$^{-1}$: its measured spectral width of

8 wave numbers is also approximately double the spectral width of that frequency shift at room temperature.

Very conspicuous also in the microphotometer records is the sharply defined peak of intensity with a frequency shift of 2176 cm.$^{-1}$ This is clearly the octave of the common frequency 1088 cm.$^{-1}$ of modes V and VI listed in Table I.

Of much greater intensity than either of the peaks mentioned above is that which can be recognised both in the spectra and in the microphotometer records as a clearly resolved pair of lines whose frequency shifts are 2460 and 2470 cm.$^{-1}$ respectively. The calculated frequency of the octave of mode III in Table I is 2478 cm.$^{-1}$ and this is sufficiently close to the position of the doublet to justify our identifying the latter with it.

Close to the doublet but clearly separated from it appear a group of rather diffuse lines whose frequency shifts are 2490, 2502 and 2520 respectively. The mean of these three shifts is 2504 and we may therefore identify the triplet of lines as being the octave of mode III in Table I whose calculated value is 2500 cm.$^{-1}$

Finally, we have a group of rather inconspicuous maxima, of which the most evident is one with frequency shift of 2255 cm.$^{-1}$ followed by a series of others with larger frequency shifts. The octave of mode IV the frequency of which is 2298 cm.$^{-1}$ lies within this range.

7. Some Concluding Remarks

Spectroscopic investigation of the scattering of light in diamond thus decisively confirms the theoretical result that its structure possesses a discrete set of normal modes of vibration with well-defined frequencies forming a sequence as indicated in Table I. Various details revealed by the study, *viz.*, the great differences in the relative intensities with which the various modes appear and the spectral splitting which some of them exhibit are also readily explicable.

The non-appearance of modes VIII and IX as frequency shifts even in the second-order scattering is not surprising. In these modes of vibration, neighbouring atoms of carbon do not approach or recede from each other but move laterally. Hence, no very sensible variations in the optical polarisability of the structural units are to be expected. *Per contra*, the approach and recession of neighbouring carbon atoms is very conspicuous in modes I, II and III and the appearance of the octaves of these modes with notable intensities is therefore in accord with expectation. That modes II and III

appear even more strongly than mode I is clearly a consequence of their degeneracies being 8 and 6 respectively as compared with the degeneracy 3 of mode I. The strength with which the peak at 2176 cm.$^{-1}$ is recorded is likewise explicable as due to the superposition of the effect of six modes having a common frequency.

That a second-order spectrum of light-scattering is at all observable becomes intelligible when it is recalled that the oscillators which are set in vibration and diffuse the incident radiation with a diminished frequency are the structural elements in the crystal. These are of extremely small dimensions and contain relatively few atoms. Hence, the absorption by them of a quantum of energy would result in vibrations of which the amplitude cannot be considered as infinitesimally small in relation to the interatomic distances. It follows that the periodic variation of optical properties resulting from the vibration would exhibit anharmonicity. Frequency shifts corresponding to overtones and combinations of the frequencies of the normal modes can therefore appear in the scattered light. The mechanical anharmonicity associated with vibrations of finite amplitude may likewise result in the splitting up of energy levels which in the harmonic oscillator approximation can be considered as identical.

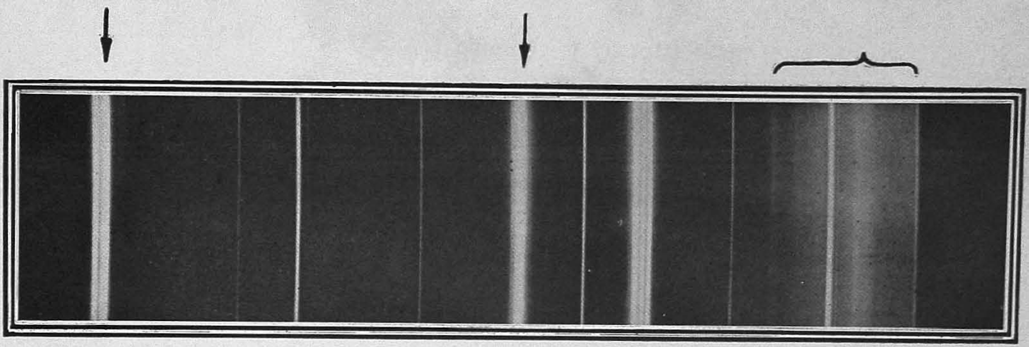


FIG. 1

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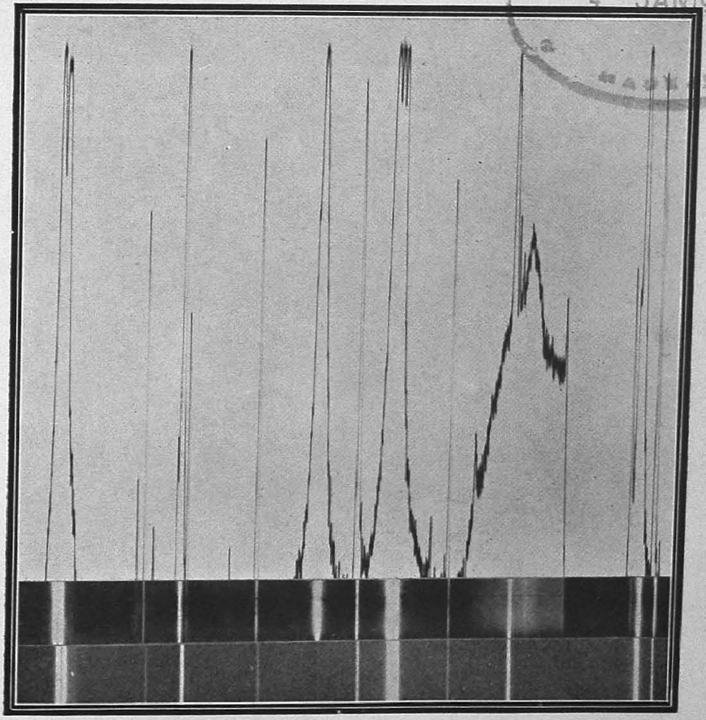

FIG. 2

Scattering of light in diamond: medium spectrograph.

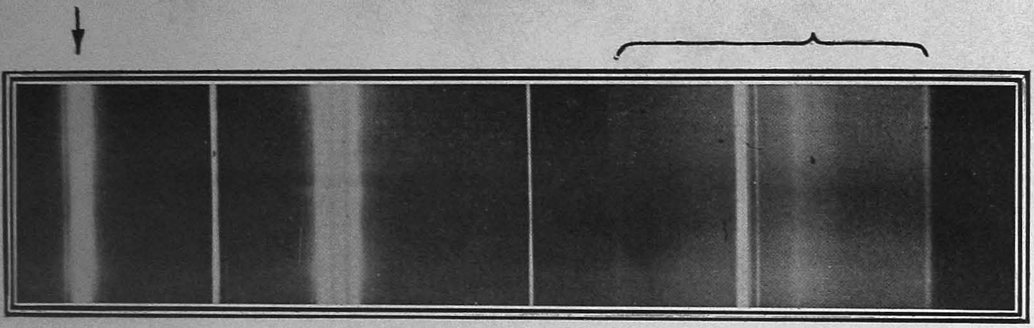

FIG. 1

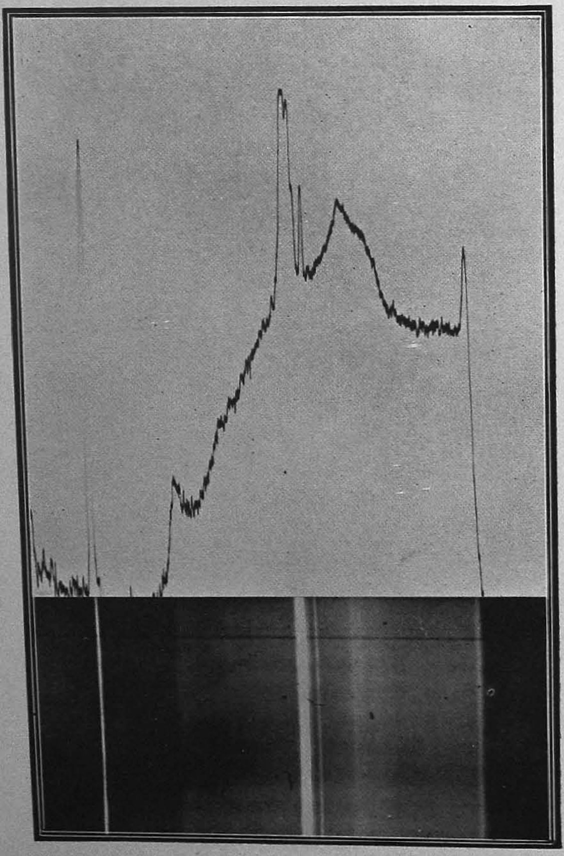

FIG. 2

Scattering of light in diamond: large spectrograph.

Reprinted from "The Proceedings of the Indian Academy of Sciences", Vol. XLIV, No. 4, Sec. A, 1956

THE SPECIFIC HEATS OF CRYSTALS

Part I. General Theory

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Received October 12, 1956

1. Introduction

The quantum theory of the specific heats of crystals proposed by Einstein in the year 1907 regards a crystal as an assembly of an immense number of harmonic oscillators with specific frequencies, the energy of vibration of which obeys the quantum rule; these oscillators form a system in thermodynamic equilibrium of which the behaviour can be described statistically with the aid of Boltzmann's theorem. Einstein identified these oscillators with the structural units (" Elementargebilde ") in the crystal and assumed that they could be grouped into sets, each set comprising a great number of oscillators characterised by a common frequency of vibration; the total number of oscillators of all sorts is taken to be thrice the number of atoms comprised in the crystal. He showed it to be a consequence of his theory that the thermal properties of a crystal would stand in the closest relationship with its spectroscopic behaviour.

The assumptions on which Einstein's theory rests are clearly justified by the physical facts of the case. For, every crystal consists of an immense number of structural units similar to each other which are capable of mechanical vibration and which by reason of their similarity may be expected to exhibit identical dynamical behaviour. The theory is, in effect, a synthesis of the results indicated by classical dynamics for such a system with the notions of the quantum theory and the basic principles of thermodynamics. It involves no inherent contradictions and can therefore claim to be a rational approach to the fundamental problems of crystal physics. The following questions, however, need to be answered before any use can be made of the theory. How are the oscillators of different sorts envisaged in the theory related to the known structure of a crystal ? How are they to be enumerated ? What is the procedure by which the characteristic frequency of each set of oscillators may be evaluated ? The present memoir concerns itself with finding the answers to these questions and thus giving form and substance to the ideas of a very general nature put forward by Einstein.

2. THE NORMAL VIBRATIONS OF CRYSTAL STRUCTURES

That the specific heat of a crystalline solid tends with rising temperature to reach a limiting value proportional to the number of atoms comprised in it is a clear indication that the theoretical approach to any explanation of the facts has of necessity to consider the subject from an atomistic standpoint. We have also to recognize the existence of interatomic forces; hence, the movements with which we are concerned are not simple translations of the individual atoms but vibrations of the atoms about their positions of equilibrium in the structure of the crystal. Any attempt to describe these vibrations or to enumerate them has necessarily to be based on the fundamental theorem in classical mechanics which states that all the possible small vibrations of a connected system of particles about their positions of equilibrium are summations of an enumerable set of normal modes; in each such normal mode, the particles of the system have all the same frequency and the same or opposite phases of vibration. Hence, any rational approach to the specific heat problem must of necessity start with a consideration of the normal modes of vibration—in the sense of the theorem just stated—of the atoms about their positions of equilibrium in the lattice structure of the crystal.

The basic principle of crystal architecture is that the structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. It follows as a necessary consequence that the normal modes of vibration of the atoms characteristic of the structure of the crystal should possess the same property. This can evidently happen in two ways, thereby enabling us to divide the normal modes into two distinct classes. In the first class of normal modes, the amplitudes as well as the phases of oscillation of the equivalent atoms which come into coincidence following a unit translation are identical. In the second class of normal modes, the amplitudes of equivalent atoms are the same but the phases are all reversed and the normal mode therefore remains the same following the unit translation. Since these two alternatives are possible for a unit translation along each of the three axes of the lattice, we have $2 \times 2 \times 2$ or 8 possible situations. Considering each of these situations separately, we proceed to write down the equations of motion of the p atoms comprised in the unit cell in terms of the $3p$ co-ordinates which determine their displacements. Since the displacements of the equivalent atoms in adjoining cells which interact with the atoms in the cell under consideration are also the same, the $3p$ equations of motion of the latter contain only $3p$ independent co-ordinates. They can therefore be completely solved, giving us $3p$ solutions for each of the eight possible situations referred to above. Thus in all, we have $24p$ solutions. $(3p-3)$

of these solutions represent normal modes of vibration of the first kind, 21 p solutions represent normal modes of the second kind and the three remaining solutions represent simple translations which have necessarily to be excluded.

The (24 p — 3) normal modes of vibration of the atoms in a crystal indicated by the theory may be regarded as the modes of *internal* vibration of the group of 8 p atoms comprised in a super-cell of the crystal lattice whose linear dimensions are twice as large as that of the unit cell consisting of p atoms. The three omitted solutions would then represent the translations along each of the three axes of the crystal lattice of the whole group of 8 p atoms included in the super-cell. Thus, we recognise that the structural unit whose dynamical behaviour is representative of the entire crystal is not the unit cell of the crystal structure, but has twice its dimensions along each of the three axes of the lattice.

Thus, following Einstein, we may regard a crystal as an assembly of (24 p — 3) sets of oscillators, each of the sets having its own distinctive frequency of vibration. The number of oscillators in each set is the same as the number of super-cells containing 8 p atoms which are included in the whole crystal. Each set of oscillators forms an assembly in thermodynamic equilibrium and its behaviour can therefore be described statistically with the aid of Boltzmann's theorem. The average energy of an oscillator in each set is given by Einstein's formula for the particular frequency. Multiplying this by the number of super-cells contained in the volume of the crystal, we obtain an expression for the energy of all the oscillators in that set. Finally, summing up the expressions thus obtained for all the (24 p — 3) sets with their respective frequencies of vibration, we obtain an expression for the thermal energy arising from the excitation of the vibrations of the atoms having precisely specifiable frequencies.

3. The Vibration Spectra of Crystals

The foregoing results may be summed up as follows. If a unit volume of the crystal contains S super-cells each including 8 p atoms, the total number of degrees of atomic freedom is 24 pS; a very large proportion of this number, *viz.*, (24 p — 3) S degrees of freedom, appears in the vibration spectrum of the crystal as sharply defined monochromatic frequencies; (3 p — 3) of these frequencies represent vibrations in which equivalent atoms contained in each super-cell have the same amplitudes and phases of vibration, while the 21 p other frequencies represent modes of vibration in which the amplitudes are the same but the phases are opposite for equivalent atoms along one, two or all three of the axes of the lattice.

We have now to consider and determine the nature of the movements represented by the 3 S degrees of atomic freedom left out in the preceding enumeration. This is also the number of degrees of freedom of translation of the S super-cells included in the crystal. Any translation of an individual super-cell would necessarily set up forces resisting such movement and also tending to displace neighbouring super-cells. We are therefore led to assume that the 3 S degrees of freedom under discussion would manifest themselves as internal modes of vibration in elements of volume of larger dimensions than our super-cell. The larger such element of volume is, the lower would be the limit of the possible frequencies of such vibration. The translations of the individual super-cells are therefore to be associated with a whole series of frequencies lying between zero and an upper limit which is set by the frequency of internal vibrations in our super-cell. To take account of the anisotropy of the crystal, we would, in general, have to assume separate upper limits of frequency for the translations along the three axes of the crystal. It is left to determine how the 3 S unassigned degrees of freedom are distributed amongst the oscillators of various frequencies lying in the permitted ranges $0 \rightarrow \nu_x$, $0 \rightarrow \nu_y$, $0 \rightarrow \nu_z$.

The problem indicated above can be dealt with and solved in a very simple manner. Consider two volume elements in the crystal which have the same shape as our super-cell and whose dimensions are respectively m and n times larger. The number of degrees of freedom of translation of these enlarged super-cells is respectively three times the number of such cells included in the volume of the crystal; the difference between them, *viz.*, $3\,S\,(1/m^3 - 1/n^3)$ would therefore be the number of oscillators whose frequencies lie between ν_m and ν_n which are respectively their lowest frequencies of internal vibration. But the principle of dynamical similarity enables us to write $\nu_m = k/m$ and $\nu_n = k/n$ where k is a constant having the dimensions of a frequency. Hence, as m approaches n, $\nu_m - \nu_n$ may be set equal to $d\nu$ and the number of oscillators whose frequencies lie between ν_m and ν_n may be written as $9\,S\,\nu^2\,d\nu/k^3$. On integrating this between zero and ν_l (the upper limit of the permitted frequencies), we should recover 3 S as the total number of oscillators, and hence k^3 is identified as ν_l^3. Accordingly, the law of distribution of frequency in the spectrum may be written as $9\,S.\,\nu^2 d\nu/\nu_l^3$ for the isotropic case. More generally, for an anisotropic crystal ν_l may be replaced by ν_x or ν_y or ν_z respectively for the three directions of translations and the numerical factor 9 is replaced by 3.

The law of distribution of the frequencies thus derived indicates that the majority of the oscillators now under consideration have frequencies not far removed from the upper limit. The same result may be expressed other-

wise by the statement that the majority of the oscillators are of very small dimensions not far removed from the lower limit, namely the dimensions of the super-cell. If, for example, we were to identify *all* the vibrations arising from the translations of the super-cell with the internal vibrations in a volume element whose dimensions are *twice* those of the super-cell, we would not be seriously in error. All except one-eighth of the 3 S degrees of freedom would be accounted for in such an enumeration; the residue omitted would represent oscillations in still larger volume elements appearing with still lower frequencies.

4. The Thermal Energy of Crystals

The atomistic approach to the specific heat problem proposed by Einstein, when fully developed, thus leads us to the following picture of the nature of the vibrations in a crystal which are the carriers of the thermal energy. The oscillating units are *not* the unit cells of the structure, but are twice as large as the unit cells in their linear dimensions; their oscillations are of two kinds, namely, those arising from their internal vibrations and those arising from their translatory movements. The oscillations of the former description appear with $(24p - 3)$ discrete frequencies of vibration, p being the number of atoms contained in the unit cells of the crystal structure. The translatory movements, on the other hand, appear with a spectrum of frequencies all of which are lower than those of the internal vibrations. These, for the most part, are concentrated near the upper limit of their permitted range; but there is a residue which tails off as a continuous spectrum to very low frequencies.

Accordingly, making use of the reasoning employed by Einstein for evaluating the average energy of an oscillator in each of the sets under consideration, we obtain the following expression for the heat content of a volume of a crystal containing N unit cells of the crystal structure as a function of the temperature, namely

$$\frac{N}{8}\left[\sum_{i=1}^{24p-3}\frac{h\nu_i}{e^{h\nu_i/kT}-1}+\frac{3}{\nu_l^3}\int_0^{\nu_l}\frac{3h\nu^3 d\nu}{e^{h\nu/kT}-1}\right]$$

The numerical factor 1/8 appears in the expression because each dynamic unit contains 8 unit cells of the crystal structure. On differentiating the expression with respect to T as usual, we get the formula for the specific heat.

The following remarks may be made regarding the numerical evaluation of the expression given above. All the $(24p - 3)$ frequencies would be distinct from each other only in the case of a completely anisotropic crystal,

If any symmetry elements are present, the number of distinct frequencies would be naturally diminished and the formula would then contain only such smaller number, but the individual terms would then have to be multiplied by their respective degeneracies. Such reduction in the number of distinct frequencies would naturally appear both in respect of the $(3p - 3)$ frequencies in which both the amplitudes and the phases are the same in adjacent unit cells and in the $21p$ others in which the phases may be opposite as already explained. As an illustration of these remarks, we may consider a case in which $p = 2$ and the crystal belongs to the cubic class and its structure consists of two interpenetrating face-centred cubic lattices. The $(3p - 3)$ distinct frequencies then reduce to a single triply degenerate frequency; the $21p$ or 42 other vibrations reduce to only eight distinct frequencies, all of which may be readily described in geometric terms related to the structure of the crystal.

Since the first term in the expression for the thermal energy is a summation extended over $(24p - 3)$ distinct modes of vibration, while the second represents only the three residual translations, it is evident that the latter would be of very minor importance relatively to the first, especially in those cases where p is very large, in other words when the crystal has a multi-atomic structure. The position is a little different when p is small, as for example, when p is equal to 1. The contribution from the second term would not then be altogether negligible in comparison with the first term. The second term also acquires some importance relatively to the first at very low temperatures. For, since the frequencies appearing in it are low, their contributions to the specific heat would survive when those due to the vibrations of the higher frequencies appearing in the first term have been effectively frozen out by reason of Boltzmann's theorem.

5. THE SPECTROSCOPIC BEHAVIOUR OF CRYSTALS

In his paper of 1907, Einstein emphasised the intimate relationship indicated by his theory between the thermal properties of crystal and their optical behaviour. It is appropriate therefore that we make a reference here to the decisive support given to the results of the theory set forth above by the experimental facts regarding the spectroscopic behaviour of crystals revealed by investigations made with a great variety of materials and by diverse techniques of investigation. We need not however dilate on this topic, since the experimental situation in this respect has been reviewed in my Lindau address, and since, moreover, the particular case of the diamond which illustrates the general principles in a very striking fashion has been dealt with in detail in a recent lecture published in these *Proceedings*.

6. Summary

In Einstein's atomistic approach to the specific heat problem, a crystal is regarded as an assembly of sets of individual harmonic oscillators, each set consisting of a great number of oscillators having a common frequency of vibration. In the present paper, this view is developed and an expression is obtained for the thermal energy of the crystal which appears as a summation of $(24\,p - 3)$ terms arising from the individual monochromatic frequencies of internal vibration of the dynamic units of the crystal structure each containing $8\,p$ atoms, with a supplementary term which takes account of the translational movements of the same units manifesting themselves as a continuous spectrum of frequencies of vibration within the crystal.

THE SPECIFIC HEATS OF CRYSTALS

Part II. The Case of Diamond

By Sir C. V. Raman

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Received October 15, 1956

In a lecture on the diamond published in the September issue of these *Proceedings* (Vol. 44, 1956, p. 99), the vibrations of the diamond structure were discussed in detail and the results of spectroscopic investigations on the nature of the vibration spectrum were also set forth. The results contained in that paper furnish us with all the material necessary for a complete theoretical evaluation of the specific heat of diamond over the entire range of temperatures for which experimental data are available. We shall now proceed to make such an evaluation and compare it with the results of the published measurements on the specific heat of diamond.

Table I gives a list of the nine characteristic frequencies of the diamond structure expressed in wave-numbers (cm.$^{-1}$), their respective degeneracies and the geometric description of the corresponding modes of vibration. The frequencies shown in the last column of the table were evaluated with the aid of the equations of motion and a set of force constants and were also independently confirmed by the results of spectroscopic investigation by several

Table I

Vibration Spectrum of Diamond

No.	Degeneracy	Description of the mode	Frequency in cm.$^{-1}$
I ..	3	Oscillation of the two interpenetrating lattices against each other	1332
II ..	8	Tangential oscillation of the octahedral planes	1250
III ..	6	Tangential oscillation of the cubic planes	1239
IV ..	4	Normal oscillation of the octahedral planes	1149
V & VI ..	(3+3)	Normal oscillation of the cubic planes	1088
VII ..	4	Normal oscillation of the octahedral planes	1008
VIII ..	6	Tangential oscillation of the cubic planes	740
IX ..	8	Tangential oscillation of the octahedral planes	621

different techniques. It is a simple matter with the aid of the table to calculate the contributions to the specific heat arising from the nine modes of internal vibration of the diamond structure. The lowest frequency appearing in the table expressed in wave-numbers, *viz.*, 621 cm.$^{-1}$ may also be properly assumed to be the upper limit of frequency in the continuous spectrum of the vibrations arising from the translations of the super-cell of the crystal structure, as explained in Part I of the present paper.

The contribution to the specific heat arising from the continuous part of the vibration spectrum can be readily evaluated on this basis with the aid of the tabulated values of the relevant functions available in "Landolt-Bornstein". Table II below shows the results of such computations. The contributions to the atomic heat arising respectively from the discrete spectrum and from the continuous spectrum are shown separately for a series of temperatures ranging from 15° to 1100° on the absolute scale. The sum of the two contributions is also tabulated.

TABLE II

Theoretical Computation of the Atomic Heat of Diamond

(Calories per gram-atom per degree)

Absolute Temperature T°	Discrete Frequencies	Continuous Spectrum	Total	Absolute Temperature T°	Discrete Frequencies	Continuous Spectrum	Total
15	..	0·00014	0·00014	200	0·4069	0·1631	0·5700
20	..	0·00033	0·00033	225	0·5894	0·1895	0·7789
25	..	0·00064	0·00064	250	0·7844	0·2124	0·9968
30	..	0·0011	0·0011	275	1·0137	0·2319	1·2456
40	..	0·0026	0·0026	300	1·2418	0·2486	1·4904
50	..	0·0051	0·0051	350	1·700	0·275	1·975
60	..	0·0088	0·0088	400	2·139	0·294	2·433
70	0·0005	0·0140	0·0145	450	2·538	0·308	2·846
80	0·002	0·0207	0·0227	500	2·892	0·319	3·211
90	0·0056	0·0290	0·0346	600	3·469	0·334	3·803
100	0·0128	0·0388	0·0516	700	3·899	0·344	4·243
120	0·0419	0·0619	0·1038	800	4·224	0·350	4·574
140	0·0957	0·0877	0·1834	900	4·465	0·355	4·820
160	0·1758	0·114	0·2898	1000	4·653	0·358	5·011
175	0·2517	0·1333	0·3850	1100	4·797	0·360	5·157

The values of the atomic heats of diamond listed in Table II are exhibited in graphical form in Fig. 1. At temperatures below 70° absolute, the curve appears to touch the axis since the very low values of the specific heats in this region cannot be represented on the scale of the graph. The values in this region are, however, of great interest, since, as will be seen from

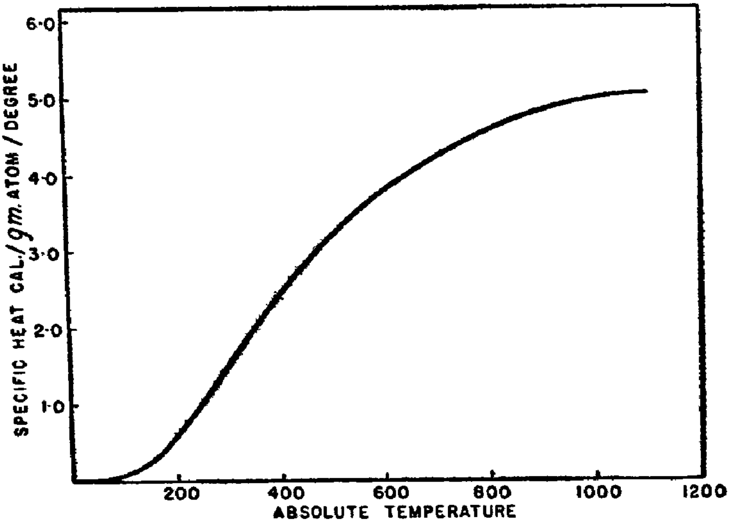

FIG. 1. The atomic heats of diamond calculated from the spectroscopic data.

Table II, they arise exclusively from the contribution of the continuous spectrum of frequencies which represents only 3 out of the 48 degrees of atomic freedom of movement of the crystal. Accordingly, the theoretical curve for this part of the temperature range has been drawn with a greatly enlarged scale for the ordinates in Fig. 2 below. Fortunately also, the specific heat of diamond in this region of temperature has been the subject of detailed investigation by Warren DeSorbo (*Journal of Chemical Physics*, Vol. 21, 1953, p. 876) and his experimental results for this very interesting region are plotted in the diagram. A gratifying agreement between theory and observation will be noticed.

The specific heat of diamond in the range of absolute temperatures from 70° to 300° was determined by K. S. Pitzer (*Journal of Chemical Physics*, Vol. 6, 1938, p. 68). The measurements by DeSorbo also cover this range. A careful inter-comparison between them shows that Pitzer's values are distinctly higher than those of DeSorbo throughout this range and that they also exhibit a scatter which is distinctly larger than the results of DeSorbo. DeSorbo's work is of later date and his data form a continuous sequence over a wider range of temperatures. For these reasons, it was felt that a comparison between theory and experiment would be more appropriately made with the results of DeSorbo. Fig. 3 below shows such comparison and here again a very satisfactory agreement emerges.

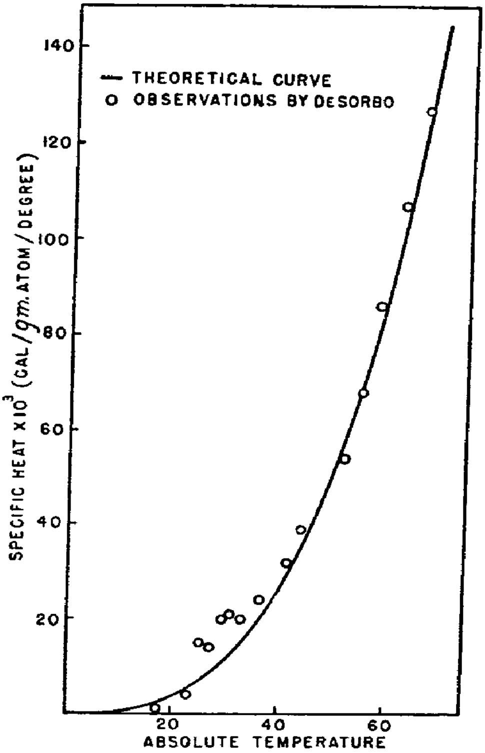

Fig. 2. Comparison between theory and experiment at very low temperatures.

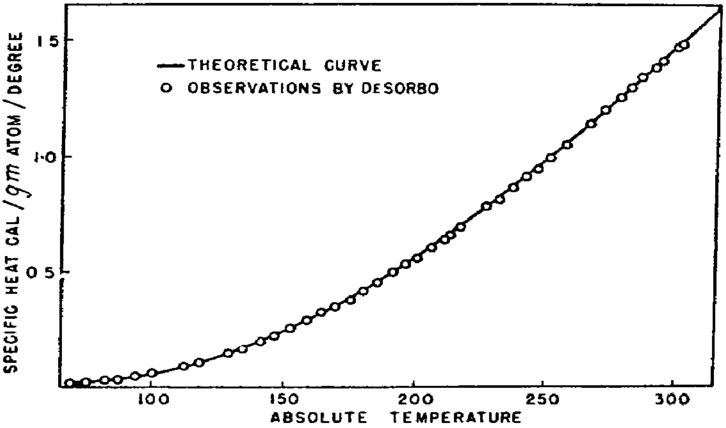

Fig. 3. Comparison of theory and experiment below room temperature.

Finally, Fig. 4 exhibits a comparison between the theoretical values and the experimental data in the temperature range from 300° to 1100° absolute covered by the determinations of Magnus and Hodler (*Annalen Der Physik*, Vol. 80, 1926, p. 808). The observed discrepancies throughout the range do not exceed two per cent. and in most cases are much less. The agreement should therefore be considered as satisfactory.

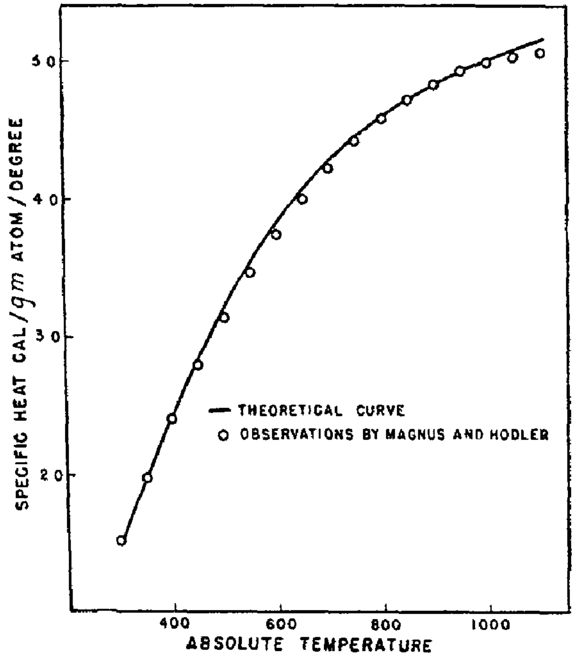

FIG. 4. Comparison between theory and experiment at high temperatures.

SUMMARY

The specific heat of diamond in the temperature range between 15° and 1100° absolute has been computed theoretically, making use of the nine spectroscopically determined vibration frequencies of the diamond structure as well as their known degeneracies, and further taking the lowest of these nine frequencies to be the upper limit of frequency in the residual continuous spectrum as explained in Part I of the paper. The results are compared with the experimental observations of DeSorbo from 15° to 300° absolute and of Magnus and Hodler from 300° to 1100° absolute. A highly satisfactory agreement between theory and experiment emerges.

Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XLIV, No. 5, Sec. A, 1956

GENERALIZED THEORY OF INTERFERENCE, AND ITS APPLICATIONS

Part I. Coherent Pencils

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Received October 30, 1956
(Communicated by Sir C. V. Raman)

§ 1. INTRODUCTION

THE investigations of which the results are presented in this paper arose during the study of certain specific problems in crystal optics. As investigators in this field are well aware, the simplest procedures for studying the optical properties of anisotropic media (*e.g.*, examination under the polarising microscope) generally involve the use and study of polarised light. The complexity of the peculiar interference phenomena exhibited and also of their customary theoretical analysis (by algebraic methods) become quite considerable even in the case of transparent optically active crystals like quartz—as may be seen by a reference to the treatises of Mascart (1891) and Walker (1904); this is because the two waves propagated along any direction in such a medium are no longer linearly polarised at right angles to one another, but are elliptically polarised. Nevertheless, the types of 'oppositely' polarised waves propagated in such media must be termed simple compared to the elliptically polarised waves propagated in *absorbing biaxial crystals.*

The remarkable interference phenomena exhibited by absorbing biaxial crystals may be easily studied by looking at an extended source through a plate (cut normal to an optic axis); a suitable material is the mineral iolite—which the author had the opportunity of investigating experimentally (Pancharatnam, 1955). (1) With the incident light polarised, and *even without the use of an analyser,* interference rings are seen, which are feeble but are nevertheless easily visible. (2) When, in addition, an analyser is also introduced, the biaxial interference figures seen are notably different from those seen in transparent crystals under the same conditions. (3) With the analyser in position and with no polariser—*i.e., with the incident light completely unpolarised*—feeble interference rings are again easily visible. (4) Finally, even when both analyser and polariser are absent, incipient traces of an interference pattern may be discerned.

Viewing these particular phenomena from a slightly broader perspective we see that their analysis is connected with certain general questions concerning the properties of two polarised beams travelling along the same direction. We shall now formulate these problems since they form the main content of the paper. The study of the effects with a polariser alone leads us to investigate the following questions: the interference of two coherent beams in different states of elliptic polarisation (§ 3); the resolution of any polarised beam into two beams in given states of polarisation—which occurs at the first face of the crystal plate (§ 4); and the composition of two coherent beams of different polarisation—at the second face of the plate (§§ 5, 6). The problem involved when an analyser is also introduced (keeping the incident light polarised) reduces to the following: the interference of two coherent polarised beams which are 'brought to the same state of elliptic vibration' by the use of a suitable analyser (§ 8). In § 9 we shall consider the addition of *n* coherent beams in different states of polarisation.

An attempt to formulate in general terms the problems associated with (3) and (4) leads rather unexpectedly into the subject of the partial coherence of polarised beams. We shall leave the discussion of this subject for Part II.

§ 2. THE POINCARÉ SPHERE AND THE STOKES PARAMETERS

For problems—such as the one we are dealing with—where we require to handle elliptic vibrations with the same facility as linear vibrations, the indirect specification of the polarisation of an elliptic vibration by giving the equation to its rectangular components is obviously unsatisfactory: the procedure not only leads to cumbersome calculations lacking in elegance, as has been pointed out by other authors, but often ceases to give physical insight into the cause of the phenomena actually observed. Two other powerful methods for specifying the state of polarisation of a beam have been used extensively—an analytical method due to Stokes (1901), and a geometrical one due to Poincaré. The conventional theoretical presentation of the subject of the 'Stokes parameters' may be found in Chandrasekhar (1949) and in Rayleigh (1902); that of the Poincaré sphere and some of its more well-known properties may be found in Pockels (1906), Walker (1904), Ramachandran and Ramaseshan (1952), and Jerrard (1954). In Part I of the present paper, only the Poincaré representation is used; and we may mention that this part constitutes in itself a self-contained derivation of the properties of the Poincaré sphere by a new procedure. The Stokes representation will be required only in Part II where the subject of partial polarisation naturally enters; but the entire subject of the Stokes representation is introduced there,

in a new manner, through the Poincaré representation itself—by developing the ideas of Fano (1949) and Ramachandran (1952).

The state of polarisation of a completely polarised beam is directly specified by the form of the ellipse traced by the tip of the displacement vector—this being invariant for a completely polarised beam, unlike the intensity and absolute phase which may be subject to statistical fluctuations. Poincaré introduced a mapping whereby any particular form of elliptic vibration is represented by a specific point on the surface of a sphere—the points on the 'Poincaré sphere' exhausting all the conceivable forms of elliptic vibrations. The definition of the mapping allows the ellipse represented by a point P to be visualised directly in terms of the longitude 2λ and latitude 2ω of the point: for λ is the azimuth of the major axis of the elliptic vibration and $\tan \omega$ the ellipticity. Alternatively the point P may be specified in cartesian co-ordinates instead of in polar co-ordinates—with the XY plane coinciding with the equatorial plane. As Perrin (1942) had observed, the *three parameters introduced by Stokes for characterising a completely polarised beam are proportional to the cartesian co-ordinates of the point P*—the constant of proportionality being the intensity of the beam which is taken as the fourth Stokes parameter.

Two elliptical vibrations whose states of polarisation are represented by diametrically opposite points on the Poincaré sphere will be said to be oppositely polarised. The conventional procedure of decomposing any elliptic vibration into two rectangular linear vibrations (represented by two diametrically opposite points on the equator) is a particular case of decomposing it into two elliptical vibrations of opposite polarisation. The fundamental property of the Poincaré sphere relates to such a decomposition (*see* Fig. 1) and is the following:—

I. *When a vibration of intensity I in the state of polarisation C is decomposed into two vibrations in the opposite states of polarisation A and A', the intensities of the 'A-component' and the 'A'-component' are* $I \cos^2 \frac{1}{2} CA$ *and* $I \sin^2 \frac{1}{2} CA$ *respectively.*

All the results proved in this paper are deduced from the above theorem. We shall not give the proof of the theorem since a proposition equivalent to the above has been proved by other authors (*see* § 8 below).

Since according to Theorem I, the sum of the intensities of the oppositely polarised component beams are together equal to the intensity I of the resultant beam we deduce the following well-known result.

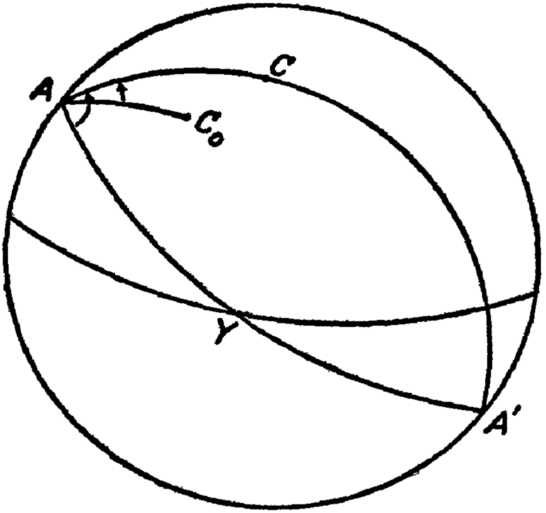

FIG. 1

II. *Two oppositely polarised beams cannot constructively or destructively interfere.*

§ 3. INTERFERENCE OF TWO NON-ORTHOGONALLY POLARISED VIBRATIONS

The interference of two *linear* vibrations not orthogonal to one another can be analysed by resolving the first vibration into two vibrations which are respectively parallel and orthogonal to the second vibration. The interference of any two elliptically polarised vibrations will now be handled in a similar manner. We shall prove the following proposition.

III. The intensity I of the beam obtained on combining two mutually coherent beams 1 and 2, of intensities I_1 and I_2 in the states of polarisation A and B respectively, will be given by the general interference formula:—

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \tfrac{1}{2}c \cos \delta \tag{1}$$

Here c is the angular separation of the states A and B on the Poincaré sphere (*see* Fig. 2). Thus $\cos^2 \frac{1}{2}c$ is a 'similarity factor' between the states of polarisation, which determines the extent of interference and which varies from unity (for identically polarised beams) to zero (for oppositely polarised beams). The significance of the 'phase difference' δ between the beams will be elucidated below.

The above relation may be obtained as follows. The vibration 2 may be replaced by two oppositely polarised vibrations—one in the state of polarisation A of the first beam, and the second in the state of polarisation A′ orthogonal to A. These vibrations (which we shall denote by 2A and 2A′ res-

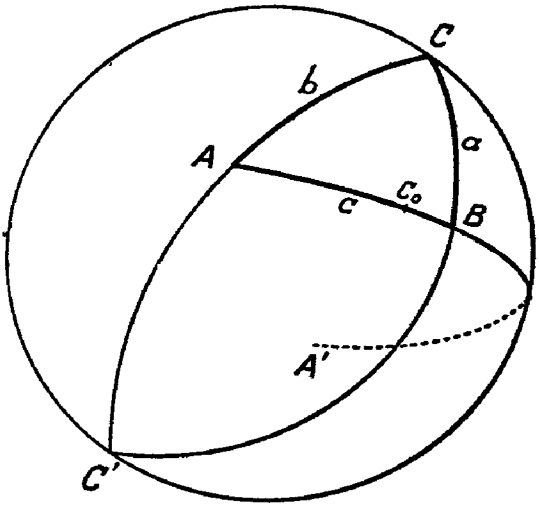

FIG. 2

pectively) will be coherent with vibration 1 and will have intensities $I_2 \cos^2 \frac{1}{2}c$ and $I_2 \sin^2 \frac{1}{2}c$ respectively (§ 2, I). The vibration 1 being in the same state of polarisation as vibration 2A (over which it has a phase advance δ, say), can be combined with it to yield a vibration (1 + 2A) of intensity

$$I_1 + I_2 \cos^2 \tfrac{1}{2}c + 2\sqrt{I_1 I_2} \cos \tfrac{1}{2}c \cos \delta$$

We are thus left with the vibration (1 + 2A) and the vibration 2A′ which are in the opposite states of polarisation A and A′. The resultant intensity I, obtained merely by adding their intensities (§ 2, II), is that given in formula (1) which we wished to deduce.

An explicit expression for the similarity factor between any two states of polarisation (in terms of the azimuths λ_1, λ_2 of the major axes and the ellipticities $\tan \omega_1$, $\tan \omega_2$ of the two vibrations) may, if necessary, be obtained from the following relation (obtained by spherical trigonometry):—

$$\cos c = \sin 2\omega_1 \sin 2\omega_2 + \cos 2\omega_1 \cos 2\omega_2 \cos 2(\lambda_2 - \lambda_1) \qquad (2)$$

It may be noted that $\cos \frac{1}{2}c$ is equal to the visibility of fringes (as defined by Michelson) obtained under the conditions $I_1 = I_2$.

In the above discussion the quantity δ has been introduced as the phase advance of the first beam over the A-component of the second beam. There are two properties of δ however which enable us to speak of it as the absolute difference of phase between the two beams themselves—though they are in different states of polarisation. In the first place we note that if the first

beam is subjected to a particular path retardation relative to the second, then δ as defined above decreases by the corresponding phase angle; in the second place we note that as long as no path retardation is introduced between the two beams, any alteration of the intensities of the two beams will not change the value of δ as defined above. Hence we will be guilty of no internal inconsistency if we make the following statement by way of a definition: *the phase advance of one polarised beam over another* (not necessarily in the same state of polarisation) *is the amount by which its phase must be retarded relative to the second, in order that the intensity resulting from their mutual interference may be a maximum.*

This phase advance is identically equal to δ, and the above definition holds only for non-orthogonal vibrations.

By picturing an elliptic vibration as being made up of its rectangular components, it becomes apparent that the coherent addition contemplated in this section, of two beams in different states of polarisation will yield a resultant beam which is also elliptically polarised. The intensity of this having been determined, the next step logically would be to determine its state of polarisation. This problem we shall relegate to § 5, and take up in the next section the converse problem which is simpler to handle.

§ 4. DECOMPOSITION OF A POLARISED BEAM INTO TWO BEAMS IN GIVEN STATES OF POLARISATION

The method of approaching the general problem described in the heading is immediately made clear by regarding the following particular case, illustrated in Fig. 3. Suppose that a *linear* vibration C has to be split into two *linear* vibrations A and B (with which it makes angles $\frac{1}{2}b$ and $\frac{1}{2}a$ respectively). The intensities of the A- and B-vibrations may be obtained by the parallelogram law; more specifically, by equating the projections of the B- and C-vibrations in the direction orthogonal to the A-vibration, we obtain the intensity of the B-vibration as proportional to $(\sin \frac{1}{2}b/\sin \frac{1}{2}c)^2$, where $\frac{1}{2}c$ is the angle between the A and B vibrations.

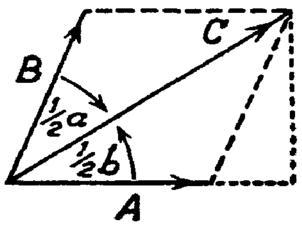

FIG. 3

By similar reasoning we shall prove the following proposition.

IV. If a beam of intensity I in the state of polarisation C is decomposed into two coherent beams 1 and 2, in the states of polarisation A and B respectively, the intensities of these beams will be given by

$$I_1 = I \cdot \frac{\sin^2 \frac{1}{2}a}{\sin^2 \frac{1}{2}c}; \qquad I_2 = I \cdot \frac{\sin^2 \frac{1}{2}b}{\sin^2 \frac{1}{2}c} \tag{3}$$

where a, b and c are the angular separations BC, CA and AB respectively (*see* Fig. 2).

To prove the proposition, we decompose each vibration into two vibrations of polarisation A and A′. The sum of the A′-components of the vibrations 1 and 2 must together be the same as the A′-component of the given vibration 3. The vibration 1, however, has no A′-component since we have chosen A′ opposite to A. Hence the A′-components of vibrations 2 and 3 are identical. Equating their intensities (as given by § 2, I) we have $I_2 \sin^2 \frac{1}{2}c = I \sin^2 \frac{1}{2}b$. Similarly, we can show that $I_1 \sin^2 \frac{1}{2}c = I \sin^2 \frac{1}{2}a$, thus establishing relations (3) above. [The expressions (3) for the intensities I_1 and I_2 could be written explicitly in terms of the constants of the elliptic vibrations by substituting the expression (2) for $\cos c$ and similar expressions, obtained by cyclic permutation, for $\cos a$ and $\cos b$. It can thus be shown that the expressions (3) are equal to the more lengthy expressions deduced directly by Stokes (*loc. cit.*).]

The beams 1 and 2 will have a definite phase relationship with one another which, as we shall see, depends in a remarkable fashion on the mutual configuration of the points A, B and C.

From (1) we have

$$\cos \delta = \frac{I - (I_1 + I_2)}{2\sqrt{I_1 I_2} \cos \frac{1}{2}c}$$

Substituting for I_1 and I_2 from (3),

$$-\cos \delta = \frac{\sin^2 \frac{1}{2}a + \sin^2 \frac{1}{2}b - \sin^2 \frac{1}{2}c}{2 \sin \frac{1}{2}a \sin \frac{1}{2}b \cos \frac{1}{2}c} \tag{4}$$

If C′ be the point diametrically opposite to C (Fig. 2), then denoting by a', b', c the sides of the triangle ABC′, we will have

$$-\cos \delta = \frac{\cos^2 \frac{1}{2}a' + \cos^2 \frac{1}{2}b' + \cos^2 \frac{1}{2}c - 1}{2 \cos \frac{1}{2}a' \cos \frac{1}{2}b' \cos \frac{1}{2}c}$$

The expression on the right-hand side is the cosine of half the solid angle subtended by the triangle C′BA at the centre of the sphere (*see* M'Clelland and

Preston, 1897, Part II, Ch. 7, p. 50, Ex. 1). Since the Poincaré sphere has unit radius, we arrive at the following unexpected geometrical result.

V. When a beam of polarisation C is decomposed into two beams in the states of polarisation A and B respectively, the phase difference δ between these beams is given by

$$|\delta| = \pi - \tfrac{1}{2}|E'| \tag{5 a}$$

where the angle $|E'|$ is numerically equal to the area of the triangle C'BA colunar to ABC. (E' is also the spherical excess of the triangle C'BA, *i.e.*, the excess of the sum of its three angles over π.)

Hitherto we have fixed the state of zero phase difference between two non-orthogonally polarised beams by the criterion that the resultant intensity produced by mutual interference should be a maximum. We can equally well use the fact (shown by relation 5 *a*) that *the beams in the state of polarisation A and B will have zero phase difference when the resultant state of polarisation C* (produced by their mutual interference) *lies on the arc directly joining A and B* (for then the colunar triangle will have the area of a hemisphere). On the other hand, the beams will be opposed in phase ($\delta = \pm\pi$), when the resultant state of polarisation C lies on the *greater* segment of the great circle through A and B (colunar triangle has zero area).

The relation (5 *a*) does not give the sign of δ—the phase advance of vibration 1 over vibration 2. We shall now resolve this ambiguity. It is clear (from considerations of continuity) that the sign of δ remains the same for all positions of the resultant polarisation C lying on any one side of the great circle AB, the magnitude of δ being between 0 and π; and that δ changes sign (without discontinuity) as the resultant polarisation C crosses from one side of the great circle AB to the other. (This is forced by the physical requirement that the addition of the beams 1 and 2 with specific intensities and a specific phase relationship should lead unambiguously to a unique state of polarisation C of the resultant beam.) We can now show that the phase advance of vibration 1 over 2 will be positive if (as is drawn in Fig. 2) the point C appears to the left of AB as we proceed from A to B on the surface of the sphere. To prove this proposition it is sufficient to show that this rule of signs is true for a *particular* pair of non-orthogonal states A and B. (For it can then be shown to hold for an adjacent pair of points A and B, from continuity arguments, and hence for *any* pair of states A and B.) As a particular case which proves the general rule, we may see in Fig. 3 that if the *linear* vibration A has a positive advance of phase over the *linear* vibration B, the resultant vibration will be left-elliptic. The results of the discussion of this

paragraph can also be summarised by using the sign convention that the area E′ of the triangle C′BA be counted positive only when the sequence of points C′BA are described in a counter-clockwise sense on the surface of the sphere. We can then write

$$\delta = \pi - \tfrac{1}{2}E' \tag{5 b}$$

§ 5. THE COMPOSITION OF NON-ORTHOGONALLY POLARISED PENCILS

When two coherent beams of intensities I_1 and I_2 (in the states of polarisation A and B respectively) are combined, the resultant state of polarisation C may be specified by the angular distances b and a of the point C from the points A and B (*see* Fig. 2). According to (3) these are given by

$$\sin^2 \tfrac{1}{2}a = \frac{I_1}{I} \cdot \sin^2 \tfrac{1}{2}c; \qquad \sin^2 \tfrac{1}{2}b = \frac{I_2}{I} \cdot \sin^2 \tfrac{1}{2}c \tag{6}$$

where I is the resultant intensity given by (1). On proceeding from A to B the point C appears to the left or right according as δ is positive or negative. An alternative method of finding the state C will be given in Part II.

The following geometrical facts are useful for qualitatively locating the state C. When the phase difference between the two beams is altered without altering the ratio of their intensities, the state C moves along the locus $\sin^2 \frac{1}{2}a/\sin^2 \frac{1}{2}b$ = constant; this is a small circle (with its centre on the great circle through AB) which cuts the arc AB internally and externally according to this ratio (*see* M'Clelland and Preston, *loc. cit.*, Part I, Ch. III, p. 66, Ex. 1). On the other hand, when the ratio of the intensities of the beams is altered without altering their phase difference, the state C moves along the locus, E′ = constant; this is a small circle passing through A and B with its centre on the great circle which is the perpendicular bisector of the arc AB (M'Clelland and Preston, *loc. cit.*, Part II, § 101). The point C is thus determined by the intersection of these two families of small circles.

§ 6. THE COMPOSITION OF TWO OPPOSITELY POLARISED BEAMS

When a polarised beam is split into two orthogonally polarised components, A and A′, the fundamental property of the Poincaré sphere enunciated in § 2, I, gives us information regarding the intensities of these components but tells us nothing about their relative phase relationship. When we wish to enquire into the latter, we run into the apparent difficulty that the state of relative phase between the two beams which could be taken as the standard or 'zero' with respect to which any additional phase differences could be measured, cannot be defined as in § 3 by their interference properties—because there is no such interference to talk of. We can however avoid the difficulty

by restricting ourselves to the following query which alone is of practical importance (*see* Fig. 1).

If, after decomposing a beam of polarisation C_0 into two oppositely polarised beams of polarisation A and A′ respectively, we retard the phase of the A′-component by an amount Δ (relative to the other), and also alter their intensities in any specified manner, what will be the resultant state of polarisation C?

To find the distance of C from A (*see* Fig. 1) constitutes no problem; for, from the first theorem (§ 2, I) itself we see that *the ratio of the* (final) *intensities of the A′ and A beams must be equal to* $\tan^2 \frac{1}{2}CA$. Our question therefore really concerns the magnitude of the angle CAC_0—regarding which we shall prove the following proposition.

VI. The angle CAC_0 is equal to the phase retardation Δ introduced.

It is remarkable that this second important property of oppositely polarised vibrations follows in the ultimate analysis as a consequence of the first fundamental property itself—for we shall prove it is a limiting case of the properties of two non-orthogonally polarised vibrations as they tend towards states of opposite polarisation.

For convenience let us regard the initial and final states of polarisation C_0 and C as given (*see* Fig. 2). We first decompose the beam of polarisation C_0 into two beams of polarisation A and B respectively, where B is chosen such that the arc AB contains C_0. By introducing a phase retardation δ between these beams of polarisation A and B, altering their relative intensities suitably and then compounding them, we can produce a beam of polarisation C. According to § 4, V, we have $\delta = \pi - \frac{1}{2}E'$, where E′ is the area of the triangle C′BA. We wish to find the limit towards which δ tends, as the state of polarisation B tends towards the state A′ opposite to A. As the point B moves towards A′ and ultimately coalesces with it, the area of the triangle C′BA obviously becomes equal to the area of the *lune* enclosed between the great circular arc AC_0A' and AC′A′, this area being $2\,\angle C_0AC'$. Hence we have

$$\Delta = \pi - \angle C_0AC' = C\hat{A}C_0$$

thus proving the required proposition. It is clear from (5 *b*) that the angle CAC_0 must be measured positive in the counter-clockwise sense as indicated in Fig. 1, in order that it may have the same sign as Δ (which is the amount by which the A-component is *advanced* in phase).

The particular property of the Poincaré sphere which has led to its extensive application in tracing the passage of polarised light through transparent

birefringent media follows as a corollary of Theorem VI above. On passage through any plate of such a medium, the emergent state of polarisation C can be obtained from the incident state C_0 by a *rotation* of the sphere by an anticlockwise angle Δ about the axis AA′, where A represents the state of elliptic polarisation of the faster of the two orthogonally polarised waves. (The author has not come across a general proof of this much-used property of the Poincaré sphere in any of the references quoted.)

A second corollary of the proposition VI is the following; when the ratio of the intensities of the orthogonally polarised beams is altered without altering their phase relationship, the locus of the resultant state of polarisation C is the great circular arc ACA′.

§ 7. Definition of the 'Phase Difference' Between Oppositely Polarised Vibrations

It will be a great convenience in connection with a later discussion to set up an arbitrary standard with respect to which the relative phase relationship between two orthogonal vibrations may be measured.

When two orthogonal linear vibrations of equal intensity combine to yield a linear vibration bisecting the right angle included between the directions OX and OX′ of their vibrations, we customarily say that the linear vibrations are in phase. (There will be no ambiguity regarding whether the vibrations are to be regarded in phase or opposed in phase, if we choose both the radii vectors OX and OX′ within the interval, $\pi/2 \geqslant \theta > -\pi/2$, with respect to a fixed radius vector Or on the wave-front.)

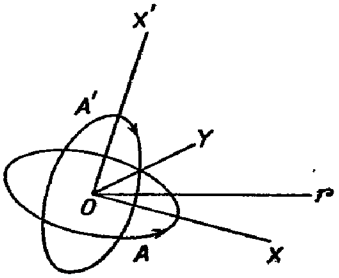

Fig. 4

In conformity with this, we may define two orthogonal elliptic vibrations of equal intensity as being in the same phase when they combine to yield a linear vibration OY bisecting the right angle included between the directions OX and OX′ of their major axes (*see* Fig. 4). The radii vectors OX and OX′ are taken parallel to the major axes of the left- and right-elliptic

vibrations respectively and are chosen such that OXX′Z forms a right-handed system—OZ being the direction of propagation. In terms of the Poincaré representation (*see* Fig. 1), the above definition has the following significance. The states of polarisation of two oppositely polarised vibrations are represented by the points A and A′ on the upper and lower hemisphere respectively, while the linear vibration OY is represented by a point Y. The point Y is one of the two opposite points on the equator at an angular distance of $\pi/2$ from both A and A′; on proceeding from A to Y the upper pole appears to the left, as indicated in the figure. The A- and A′-components of the vibration Y (and hence of any vibration represented by a point on the great circular arc AYA′) are defined to be in the same phase.

The case of opposite circular vibration is not covered in the above definition. We may define two such vibrations of equal intensity to be in the same phase when they yield a linear vibration OY parallel to a fixed radius vector Or on the wave-front.

The phase advance of one polarised vibration A over an orthogonally polarised vibration A′ is then equal to the angle CAY (measured positive in the counter-clockwise sense), where C represents the resultant state of vibration obtained on compounding the two. Henceforward we may speak of any one polarised beam as having a definite phase advance δ over another coherent polarised beam without implying that the two beams are non-orthogonally polarised.

§ 8. Interference of the Components of Two Polarised Beams Transmitted by an Analyser

It is well known that light of any arbitrary elliptic polarisation C′ may be extinguished by means of an appliance consisting of a suitably oriented quarter-wave plate followed by a linear analyser at the proper setting; when light of the opposite polarisation C is incident on the same appliance the *intensity* of the transmitted light will be equal to that of the incident—as may be directly shown (Stokes, 1901), without using any property of the Poincaré sphere. Any appliance having both the above properties will be referred to as an *analyser C.*

Since light of any other polarisation P may be decomposed into two coherent beams of polarisation C and C′, the intensity transmitted by an analyser C will be equal to the C-component of the incident beam. If we assume the fundamental Theorem I, § 2, it follows that an analyser C transmits a fraction $\cos^2 \frac{1}{2}PC$ of the intensity of light of polarisation P. Conversely, one of the simplest proofs of the fundamental Theorem I, lies in the direct analytical

proofs of this property of an analyser given by Fano (1949) and also by Ramachandran and Ramaseshan (1952).

As was pointed out in the Introduction, the problem to be now discussed arises when we wish to consider the phenomena exhibited by a plate of an absorbing biaxial crystal when kept between a polariser and an analyser. Emerging from the crystal plate along any particular direction will be a coherent mixture of two beams 1 and 2. Let their states of polarisation be A and B, their intensities I_1 and I_2, and let the phase advance of the first beam over the second be δ. (The state of polarisation of the resultant beam will not be required here and will *not* be denoted by C.)

In order to compute the intensity transmitted by an analyser C, we first resolve each of the two vibrations into the opposite states of polarisation C and C′ (*see* Fig. 2). The C-components of the beams of polarisation A and B will have intensities $I_1 \cos^2 \frac{1}{2}b$ and $I_2 \cos^2 \frac{1}{2}a$ respectively (§ 2, I). Since these components will have some definite phase difference δ', say, they can interfere. Hence the resultant beam obtained by combining the beams 1 and 2 will have a C-component whose intensity I_C is given by

$$I_C = I_1 \cos^2 \tfrac{1}{2}b + I_2 \cos^2 \tfrac{1}{2}a + 2\sqrt{I_1 I_2} \cos \tfrac{1}{2}a \cos \tfrac{1}{2}b \cos \delta' \qquad (7)$$

Similarly the C′-components of the beams 1 and 2 will have intensities $I_1 \sin^2 \frac{1}{2}b$ and $I_2 \sin^2 \frac{1}{2}a$ respectively, and a definite phase difference δ'', say. Hence the C′-component of the resultant beam will have an intensity $I_{C'}$, given by

$$I_{C'} = I_1 \sin^2 \tfrac{1}{2}b + I_2 \sin^2 \tfrac{1}{2}a + 2\sqrt{I_1 I_2} \sin \tfrac{1}{2}a \sin \tfrac{1}{2}b \cos \delta'' \qquad (8)$$

Since an analyser transmits only the intensity I_C it remains to determine δ' in terms of the phase difference between the beams 1 and 2, and the analyser position C.

Now δ' represents the phase advance of the C-component of the beam of polarisation A over the C-component of the beam of polarisation B; while δ'' is the phase advance of the C′-component of the beam of polarisation A over the C′-component of the beam of polarisation B. Hence *it follows from a consideration of VI*, § 6, *that* $\delta'' - \delta' = \pm \hat{C}$ (where the positive sign has to be taken if C lies on the side of AB shown in Fig. 2). Furthermore, the intensity I of the resultant beam obtained on compounding 1 and 2 is equal to the sum of the intensities of the C- and C′-components (§ 2, II).
Hence adding (7) and (8)

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\{\cos \tfrac{1}{2}a \cos \tfrac{1}{2}b \cos \delta' + \sin \tfrac{1}{2}a \sin \tfrac{1}{2}b \cos(\delta' \pm C)\}$$

Expanding $\cos(\delta' \pm C)$, it can be shown by applying the standard expressions for the spherical excess of a triangle (M'Clelland and Preston, *loc. cit.*, Part II, p. 37, Art. 104) that the above relation reduces to

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\tfrac{1}{2}c\cos(\delta' + \tfrac{1}{2}E)$$

where E represents the area of the triangle ABC itself (counted positive or negative according as the sequence of points A, B, C describe the periphery of the triangle in the counter-clockwise or clockwise sense). The intensity I is also given directly in terms of the phase difference δ between the beams 1 and 2 by the expression (1) of § 3. Comparing the two we get the value of δ' to be substituted in (7):

$$\delta' = \delta - \tfrac{1}{2}E \tag{9}$$

VII. Hence when a mixture of two coherent beams of intensities I_1 and I_2 in the states of polarisation A and B respectively, is incident on an analyser C, the transmitted intensity I_C is given by

$$I_C = I_1\cos^2\tfrac{1}{2}b + I_2\cos^2\tfrac{1}{2}a + 2\sqrt{I_1 I_2}\cos\tfrac{1}{2}a\cos\tfrac{1}{2}b\cos(\delta - \tfrac{1}{2}E) \tag{10}$$

where δ is the phase advance of the beam of polarisation A over the other, a, b and c being the angular sparations BC, CA and AB respectively and E the area of the triangle ABC.

It is to be noted that the above result must also hold in the limiting case when the two beams incident on the analyser are in the orthogonal states of polarisation A and A'. In this case, if AYA' be the great circular arc (Fig. 1) with respect to which the phase difference δ is measured (ref. § 7), then E (which now becomes the area of the lune AYA'CA) is equal to twice the angle CAY. The expression (9) may in this case be further simplified by the substitution $\cos\tfrac{1}{2}a = \sin\tfrac{1}{2}b$.

§ 9. THE ADDITION OF *n* COHERENT BEAMS

Suppose a mixture of 3 coherent beams of polarisation A_1, A_2, A_3 is incident on an analyser C. Let $2\theta_i$ denote the length of the arc CA_i, δ_{ij} denote the phase *lag* of the beam i over the beam j, and E_{ij} be the area of the triangle A_iCA_j. We have obviously

$$\delta_{ij} = -\delta_{ji}; \qquad E_{ij} = -E_{ji} \tag{11}$$

The C-component of the first vibration may be written as $\sqrt{I_1}\cos\theta_1\,\mathbf{c}\,e^{i\omega t}$ where $\mathbf{c}\,e^{i\omega t}$ is a vibration of unit intensity in the state of polarisation C†.

† The components of the vector **c** are the complex amplitudes of the components of the elliptic vibration.

If $A\,c\,e^{i\omega t}$ denote the C-component of the resultant vibration obtained on compounding the three vibrations, then according to (9) we will have,

$$A = \sqrt{I_1}\cos\theta_1 + \sqrt{I_2}\cos\theta_2 \exp i\,(\delta_{12} - \tfrac{1}{2}E_{12})$$
$$+ \sqrt{I_3}\cos\theta_3 \exp i\,(\delta_{13} - \tfrac{1}{2}E_{13})$$

Since the phase lag of the C-component of the second beam over the C-component of the third is according to (8), given by $(\delta_{23} - \tfrac{1}{2}E_{23})$ we have

$$-(\delta_{23} - \tfrac{1}{2}E_{23}) = (\delta_{12} - \tfrac{1}{2}E_{12}) - (\delta_{13} - \tfrac{1}{2}E_{13}) \qquad (12)$$

with similar expressions connecting all the δ_{ij}. Hence the intensity I_C transmitted by an analyser C being equal to AA^*, will be given by

$$I_C = \Sigma\, I_i \cos^2\theta_i + \sum_{i\neq j} \sqrt{I_i I_j}\cos\theta_i\cos\theta_j\cos(\delta_{ij} - \tfrac{1}{2}E_{ij}) \qquad (13)$$

The resultant intensity I of the beam obtained on compounding the three beams will be equal to the sum of the intensities I_C and $I_{C'}$, where $I_{C'}$ is the intensity transmitted by the orthogonal analyser C′. The resultant intensity can in this manner be shown to be given by

$$I = \Sigma\, I_i + \sum_{i\neq j} \sqrt{I_i I_j}\cos\tfrac{1}{2}c_{ij}\cos\delta_{ij} \qquad (14)$$

It is obvious that the same argument holds when there are a mixture of *n* coherent beams; the formula (13) gives the intensity transmitted by an analyser C, while (14) gives the resultant intensity. The state of polarisation of the resultant beam will be deduced incidentally in Part II. We may here merely note that by deducing the intensity transmitted by any analyser C we have a method of deducing the resultant polarisation of the beam: for example, we could find the particular analyser for which the transmitted intensity is zero.

In conclusion the author wishes to express his deep sense of indebtedness to Professor Sir C. V. Raman, F.R.S., N.L., without whose encouragement this work could not have been written.

§ 10. Summary

The superposition of two coherent beams in different states of elliptic polarisation is discussed in a general manner. If A and B represent the states of polarisation of the given beams on the Poincaré sphere, and C that of the resultant beam, the result is simply expressed in terms of the sides, *a*, *b*, *c* of the spherical triangle ABC. The intensity I of the resultant beam is given by:

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\tfrac{1}{2}c\cos\delta;$$

the extent of mutual interference thus varies from a maximum for identically polarised beams ($c = 0$), to zero for oppositely polarised beams ($c = \pi$). The state of polarisation C of the resultant beam is located by $\sin^2 \frac{1}{2}a = (I_1/I) \sin^2 \frac{1}{2}c$ and $\sin^2 \frac{1}{2}b = (I_2/I) \sin^2 \frac{1}{2}c$. The 'phase difference' δ is equal to the supplement of half the area of the triangle C′BA (where C′ is the point diametrically opposite to C). These results also apply to the converse problem of the decomposition of a polarised beam into two others.

The interference of two coherent beams after resolution into the same state of elliptic polarisation by an elliptic analyser or compensator is discussed; as also the interference (direct, *and* after resolution by an analyser) of n coherent pencils in different states of polarisation.

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Reprinted from J. Madras Univ., B, 27, No. 1. Centenary Number, 1957.

The Optical Behaviour of Polycrystalline Solids

BY

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(Memoir No. 89 from the Raman Research Institute, Bangalore 6)

ABSTRACT

The paper discusses the influence of the factors which determine the penetration of light into a polycrystalline solid, viz. the birefringence of the crystallites, their size and shape and their relative orientations. The results of the theoretical discussions are compared with the facts of observation. Five X-ray diagrams are also reproduced which exhibit the relation between the structure and optical behaviour of polycrystalline media in particular cases of interest.

1. *Introduction.*

As examples of polycrystalline solids which by reason of the desirable properties they possess have been extensively used for the fashioning of works of art may be mentioned especially the following minerals: marble, alabaster, chalcedony and jade. Visual observations supplemented, where necessary, by examination of thin slices under the polarisation microscope and the use of X-ray diffraction techniques reveal that individual specimens of these minerals may be widely different in regard to the size and shape of the crystallites of which they are composed and the manner in which these crystallites are disposed within the solid. Alongside of these differences and obviously related to them are noticed some striking differences in the optical characters of the specimens. As the external appearance of a finished work of art is influenced a good deal by such differences, it is not without interest to discuss in some detail the nature of the relationship between the structure and the optical behaviour of polycrystalline solids in general.

In all the cases mentioned, the basic substance is a transparent crystalline solid and accordingly the aggregate could also have been expected to be free from colour. Though this is so in some instances, it is not always the case. Indeed, the presence of some favoured colours often enhances the value of the material very greatly. The nature of the intrusive material res-

ponsible for such colour and the manner in which it is diffused through the substance and influences its optical behaviour are questions of considerable interest, but we shall not enter into them here.

It should be mentioned that the structure of polycrystalline solids and its relation to their optical behaviour has been the subject of both theoretical and experimental investigations by the present writer and his collaborators and the results have been reported in detail in some earlier memoirs of this Institute. In the present publication it is proposed to summarise broadly the results which have emerged from these studies and in addition to present some fresh observational material.

The five illustrations accompanying the present paper are X-ray-diffraction photographs of some interesting specimens recorded by Mr. A. Jayaraman at this Institute. In each case, the structure revealed by the X-ray diagram is found to be very clearly related to the optical characters exhibited by the specimen. We shall return to these diagrams and their significance later in the paper.

2. *Theoretical Considerations.*

If no extraneous material be present in a polycrystalline solid and its optical heterogeneity arises solely by reason of the varying orientations of the crystallites, the birefringences of the latter would give rise to a diffusion of the light in its passage through the material. At each incidence of the light on an intercrystalline boundary, it would be reflected and refracted and hence all trace of the original direction of propagation of the light would quickly disappear. After the passage of the light through a sufficient number of crystallites, a state of affairs would establish itself in which we have a diffusion in all directions, forwards and backwards as well as laterally. The greater the birefringence of the material, the fewer would be the number of intercrystalline boundaries needed for such a situation to establish itself. We may visualize the resulting phenomena by imagining a pencil of light to fall normally on a restricted area in the plane face of a block of the material. The observable results would then depend upon the various factors involved, namely the thickness of the block, the size of the crystallites and the magnitude of their birefringence.

In the absence of any absorbing material and if the thickness of the block be sufficiently great, all of the incident light must necessarily be turned back towards the original source of light and would re-emerge from the same face spread out from a much larger area than that on which it is originally incident. On the other hand, if the thickness of the block be not too great, part of the incident radiation would also emerge from the rear face of the block spread out over a large area. In each case, the observable effects would be profoundly influenced by the size of the crystallites. The smaller the crystallites are, the more quickly would the incident light be turned back towards the source and the less, therefore, would be the depth of the penetration of the light into the medium. The presence of any absorbing material in the solid would necessarily modify the observable results to a very great extent.

3. *Diffraction Phenomena.*

While the arguments set forth above based on geometrical optics may be adequate when the crystallites are of sufficiently large dimensions and the birefringence of the material is also fairly large, they would cease to be adequate and would fail to describe what is actually observed when the reverse is the case, i.e., when the crystallites are of small dimensions and the birefringence which they exhibit is also small. In the latter circumstances, the matter has necessarily to be considered from the standpoint of the wave theory of light, and the results indicated by such theory are very different indeed from those indicated by geometrical optics.

We may here broadly indicate the lines on which the problem can be handled on the basis of the wave theory. If the birefringence of the material be sufficiently small, the diffusion of light in its passage through it may be considered as arising from the varying retardations in phase of the light waves in traversing the differently oriented crystallites. Provided that the product of the linear dimension of each crystallite and of its birefringence is sufficiently small, we can regard the waves as moving undisturbed through the medium except for the changes of phase occurring over different areas of the wave-front; such changes may be regarded as being additive in depth and hence capable of being summed up over the whole of the path through a slab of the material, provided that the thickness of the latter is not too great. The wave-

front emerging at the rear surface of the block would thus exhibit fluctuations in phase over its area. The final observable effect may then be determined by the usual methods of diffraction theory.

The foregoing brief exposition ignores certain difficulties, namely, that inside each crystallite there would be two possible directions of vibration for which the refractive indices are different and these two directions would vary from crystallite to crystallite owing to their random orientations. This difficulty, however, may be circumvented by assuming that the light incident on the block is plane-polarised and that all the crystallites are so orientated that this original direction of vibration in the wave-front is preserved in its passage through the block, the operative refractive index for any one crystallite being one of its three principal values chosen at random. Such an assumption has the great advantage that it greatly simplifies the formulation and solution of the problem while retaining its essential features. Further, by assuming the probabilities of the three different orientations to be different, we can also determine the optical behaviour of polycrystalline solids in which the crystallites are not orientated at random but prefer certain directions. What the solution of the problem gives us is the intensity of the light regularly transmitted through the polycrystalline plate. This appears as an exponential function in which the argument has a negative sign and is directly proportional to the thickness of the plate and to the size of the crystallites and also to a quantity depending on the differences between the three refractive indices which is a measure of the birefringence; it is also inversely proportional to the square of the wave-length of the light. From the theory it follows that the light emerging from the block would be polarised in the same fashion as the light incident on the first face. The theory also shows that if the crystallites have no preferred orientation, the transmission coefficient is independent of the direction of vibration in the incident light. If, however, the crystallites are preferentially orientated, the intensity of the light emerging from the plate would vary with the circumstances, viz., with the relative probabilities of the three permitted orientations. In particular cases of this kind, e.g., when all the crystallites are orientated along a fibre axis which is also the optical vibration direction, the transmission may be actually complete.

We may summarise the foregoing by stating that on the basis of the assumptions made, the light incident on a plate of polycrystalline material would emerge from it greatly enfeebled in

intensity but retaining its primitive state of polarisation. The fraction of the light regularly transmitted for a given thickness of the material would increase with diminishing size of the crystallites and would reach the limiting value of unity if they are sufficiently small. This result is precisely the opposite of that indicated by the geometrical theory according to which diminishing particle size would result in greater opacity. These two contrasting results may be regarded as valid respectively in the limiting cases of a very weak and of a very strong birefringence.

The energy that disappears from the regularly transmitted light would appear as diffracted radiation. Its distribution of intensity in different directions would be determined by the factors entering into the problem, namely, the size of the crystallites, the thickness of the plate, the birefringence of the material and finally the wave-length of the light. It is a consequence of the special assumptions made regarding the orientation of the crystallites that the diffracted radiation would be polarised in the same manner as the incident and emerging pencils. It is not, however, to be expected that this particular result would represent the actual facts of the case. As a consequence of the unrestricted randomness of the orientation of the crystallites, the diffused or diffracted radiation would necessarily be depolarised to a greater or less extent. The greater the birefringence of the material or the thickness of the plate traversed, the more complete would be such depolarisation.

It is a particular consequence of the theory that if unpolarised light be incident on a plate of material having a fibrous structure and of sufficient thickness, the regularly transmitted beam would be completely polarised on emergence, while the rest of the light would appear as a fan of diffracted rays in the plane perpendicular to the fibre axis and polarised predominantly in the perpendicular direction. It has also to be remarked that a fibrous structure of the medium is favourable to the appearance of a regularly transmitted pencil. The same material with crystallites randomly orientated might not exhibit any transmission at all, but only a diffusion of light in various directions surrounding that of the incident pencil. Finally, we may remark that since these phenomena arise by reason of wave-optical considerations depending on the wave-length of the light, the transmitted light whenever it is observable should exhibit a reddening which increases progressively with the thickness of the material traversed.

4. *Some Illustrations of the Theory.*

Marble which in its purest forms consists of calcite furnishes excellent illustrations of the optical behaviour of a polycrystalline medium consisting of strongly birefringent crystallites. The influence of the grain size on the penetration of light into the material indicated by the theory is readily confirmed by observations with different specimens. A very interesting fact is that the light diffused by marble both backwards and forwards exhibits a surprisingly rich redness even when the marble itself is only of a faintly pinkish colour.

Alabaster which consists of randomly orientated crystallites of gypsum affords good illustrations of the behaviour of a polycrystalline medium in which the crystallites have only a feeble birefringence. The size of the crystallites can of course be readily determined by cutting a thin section and viewing it under a polarising microscope. The relationship between the size of the crystallites and the optical behaviour of the material can be readily confirmed by viewing a bright source of light through a slice of alabaster mounted between microscope cover-slips with a little Canada balsam. Only with the thinnest sections is a true optical transmission observable. This appears surrounded by a diffusion halo exhibiting streaky colours in white light. The depolarisation of the halo and the polarisation of the regularly transmitted light when the incident light is polarised are also readily confirmed by observation.

The X-ray diffraction diagram of alabaster depends very much on the size of the crystallites which it contains. Unless the alabaster is very fine-grained, a collection of spots only vaguely indicative of a ring pattern is obtained. Very different is the picture shown in Fig. 3 in Plate I which shows a readily recognizable ring system, though spotty in character. This was obtained with a very fine museum piece exhibiting a remarkably high degree of translucency.

Fig. 2 in Plate I is an X-ray diagram recorded with a dish of Chinese origin stated to be of jade, but not really so. The material was colourless and exhibited a high degree of translucency. The extremely small size of the crystallites of which it is composed is evident from the X-ray diagram.

Fig. 1 in the same Plate is the X-ray diagram obtained by passing a beam of X-rays through a plate of a white porcelain-like

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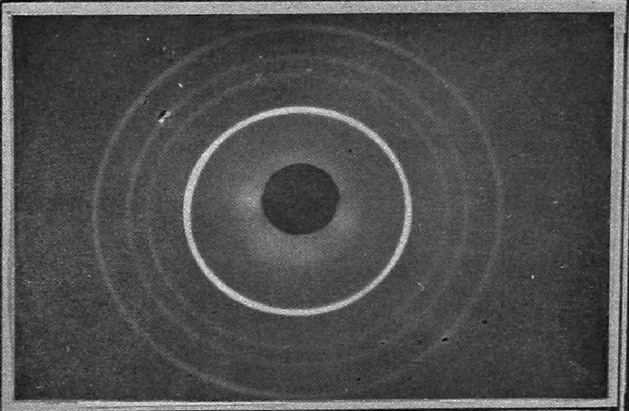

Fig. 1

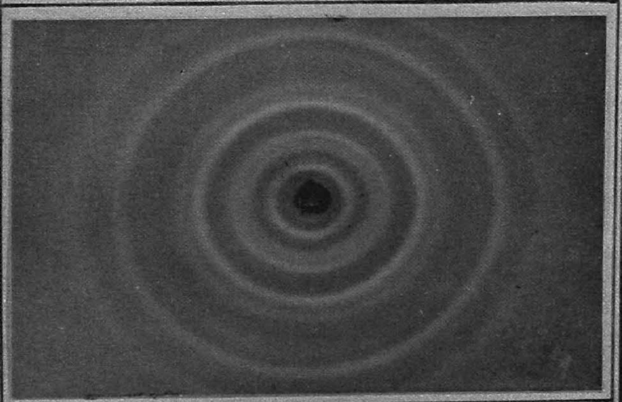

Fig. 2

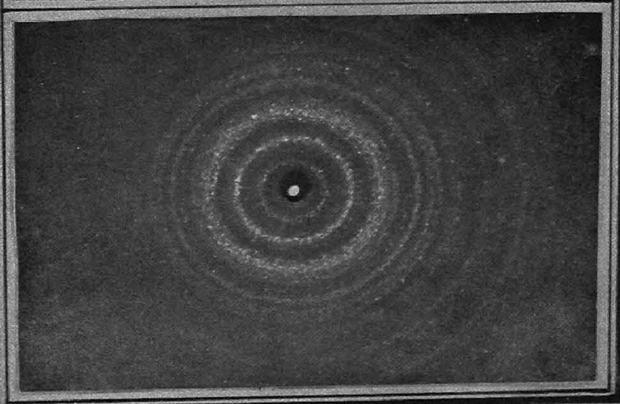

Fig. 3

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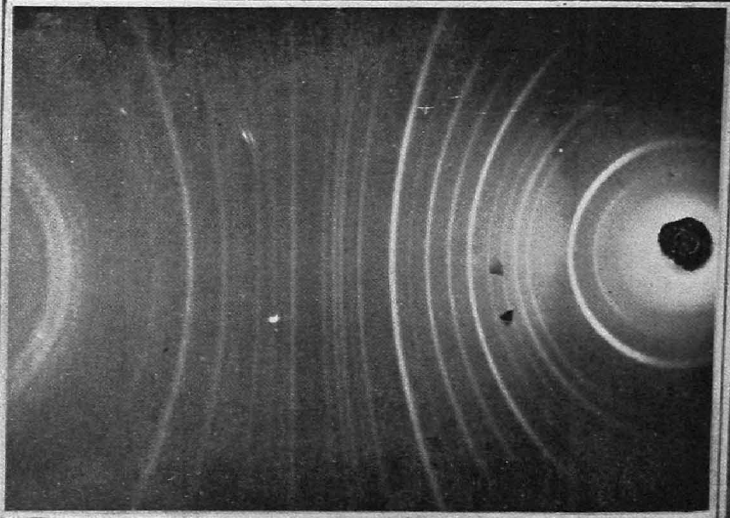

Fig. 4

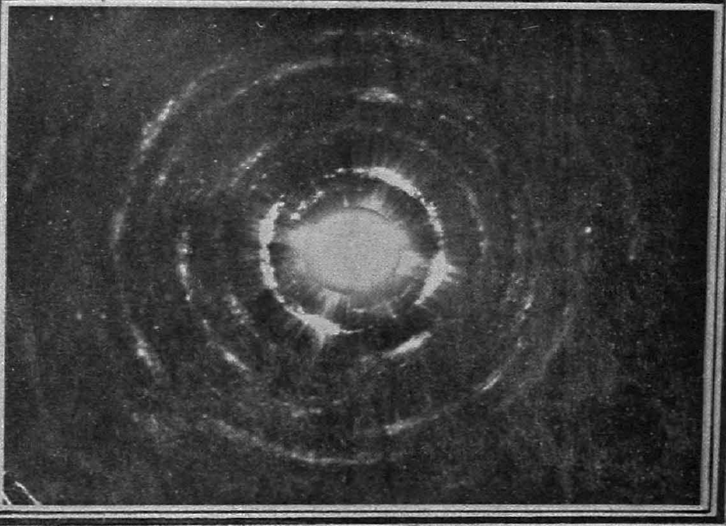

Fig. 5

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material which was cut out from a block of agate and which was identified as α-cristobalite by its X-ray pattern. The extreme fineness of the particles of the material is evident from the X-ray diagram. A source of white light seen through the plate is visible, but appears of a deep red colour. The material thus furnishes an excellent example of a polycrystalline medium consisting of a birefringent material which nevertheless exhibits a true optical transmission by reason of the small size of the crystallites.

The phenomena arising from the propagation of light through a medium with a fibrous structure are beautifully illustrated by observing a source of light through a polished plate of chalcedony. They exhibit in a very conspicuous manner the various features indicated by the theory. It should be emphasized that chalcedony exhibits large variations in its structure and these correspond to striking differences in optical behaviour. Two extreme cases are illustrated respectively by Figs. 4 and 5 in Plate II. The first is an X-ray diagram recorded with a specimen of agate which exhibited only translucency but no real transmission of light. It will be seen from the X-ray diagram that this material consisted of extremely fine particles. Fig. 5, on the other hand, is an X-ray diagram of a specimen of chalcedony showing a coarsely fibrous structure. A source of light could easily be seen in perfect focus through the plate though much dimmed in intensity and reddened in colour. The transmitted light was found to be completely polarised, and this was evidently a consequence of the fibrous structure revealed by the X-ray pattern and also evidenced by the streams of diffracted light seen surrounding the image of the source.

Reprinted from "The Proceedings of the Indian Academy of Sciences,"
Vol. XLIV, No. 6, Sec. A, 1956

QUANTUM THEORY AND CRYSTAL PHYSICS*

By Sir C. V. Raman
(*Memoir No. 90 from the Raman Research Institute, Bangalore-6*)
Received December 8, 1956

1. Introduction

The physics of the twentieth century differs fundamentally from the physics of the nineteenth mainly because of two theories known respectively as the Quantum Theory and the Theory of Relativity which form an integral part of its scheme of thought. It is these two theories that have enabled a far deeper understanding of the nature of the physical world to be attained than was possible at the end of the last century. One must here acknowledge the work of Albert Einstein who played the leading role in the development of both of these theories. His publications during the first two decades of the present century bear on every page the imprint of a powerful and penetrating intellect. Even after this lapse of years, the physicist of today will find the study of those papers a profitable and stimulating experience. Indeed, a good deal of what I have to say in this address only reflects the results of such a study in relation to the fundamental problems of the crystalline state of matter—a subject which has deeply interested me for several years past.

2. Origin of the Quantum Theory

The quantum theory arose from the attempt to explain the characters of the radiation which emerges from the window of an enclosed furnace heated to high temperatures. As is well known, the total intensity of such radiation increases rapidly with rise of temperature of the furnace. Simultaneously, there is a shift of the spectral maximum of intensity towards higher frequencies, as is indeed evident from the progressive change in colour of the radiation. Thermodynamic considerations indicate that this shift should occur in such a manner that the spectral frequency at the point of maximum intensity should be directly proportional to the absolute temperature of the furnace. Quantitative measurements confirm that this is the case and show that the changes in the intensity as well as in the spectral character of the radiation with rise of temperature agree with a formula for the spectral intensity in which the cube of the spectral frequency appears multiplied by

* Presidential address to the Indian Academy of Sciences at Waltair on the 26th December 1956.

an exponential function of a type made familiar by Boltzmann's well-known principle. The argument of the exponential function is negative and has as its numerator the spectral frequency multiplied by one universal constant and as its denominator the absolute temperature multiplied by another universal constant. A small but important modification secures a much more satisfactory agreement between the formula and the facts of observation. In the modified expression, the exponential has the same argument with a positive sign and now appears in the denominator with unity subtracted from it. This is the celebrated Planck formula except for a multiplying numerical factor.

3. EINSTEIN'S DERIVATION OF THE PLANCK FORMULA

Einstein gave a physical interpretation of the Planck formula and also showed how the formula could be derived on the basis of simple physical considerations. He interpreted the formula to mean that radiation of all frequencies is emitted and absorbed by material bodies in discrete quanta of energy proportional to their respective frequencies. He also showed that the radiation formula follows very naturally if we assume that the energy of the material particle which emits the radiation is itself quantised, in other words, its energy of vibration alters by successive steps, each of which is equal to the quantum of radiation energy which is emitted in the process.

A more complete and logically satisfying derivation of the Planck radiation formula was given by Einstein ten years later, *viz.*, in 1917. In that paper, the notion of probability which in the quantum theory replaces the determinism of the older physics finds a prominent place. Instead of assuming the radiator to be a harmonic oscillator as in his paper of 1907, Einstein dealt with the most general case of an oscillator which has a number of discrete energy levels. The probability of its being present in any one of them is expressed by the product of the inherent statistical weight characteristic of the level multiplied by the appropriate thermodynamic probability factor. The latter takes the form of an exponential function with a negative argument equal to the energy of the state divided by the product of the absolute temperature and the Boltzmann constant. Einstein then considers the probability of three different kinds of elementary processes occurring in any given small time interval. The first is a spontaneous transition from the higher to a lower state of energy with emission of radiation as contemplated in Bohr's theory of spectra; the second is a transition of the same nature but now induced by the presence of an external radiation field; the third is a transition from the lower to the higher energy state also induced by the external field. The probabilities of the two latter transitions are taken as proportional

to the energy density in the surrounding radiation field. A transfer of energy from the oscillator to the field and an absorption of energy from the field by the oscillator are involved respectively in the two processes. In a steady state of affairs, the probabilities of transition in the two opposite directions must necessarily balance each other. These considerations lead at once to the Planck radiation formula.

4. The Crystal as an Assembly of Oscillators

The foregoing exposition of Einstein's original ideas is intended to furnish a theoretical background for a consideration of the fundamental properties of the solid state which is the subject of the present address. Elementary processes closely analogous to those contemplated in Einstein's paper of 1917 successfully describe the phenomena actually observed when a beam of monochromatic light traverses a crystal and the light diffused in its interior is examined spectroscopically. We observe in the spectrum of the scattered light sharply defined lines with frequencies both higher and lower than that of the incident radiation. The ratio of the intensities of each such pair of lines having equal spectral displacements in opposite directions is found to be expressed correctly by a Boltzmann factor corresponding to the change of frequency multiplied by Planck's constant, this again being multiplied by the fourth power of the ratio of the two spectral frequencies. These facts indicate that the displaced frequencies arise from transitions from a higher to a lower energy state and *vice versa* induced in the elementary oscillators comprised in the crystal by the incident radiation. We are thus naturally led to regard the crystal as an assembly of a great number of oscillators which form a system in thermodynamic equilibrium. The thermal energy of the crystal may then be equated to the sum of the thermal energies of all the oscillators of the different sorts of which it is composed.

It is evident from what has just been stated that the specific heats of crystals stand in the closest relation to their spectroscopic properties. The first step in the theoretical evaluation of the thermal energy of the crystal is accordingly to identify and enumerate the oscillators of which it is composed and to discover and specify the energy states which they can occupy.

5. The Oscillators and Their Energy Levels

To begin with, we may provisionally identify the oscillators with whose behaviour we are concerned with the groups of atoms present in the unit cells of the crystal structure. To discover the energy levels which these oscillators can occupy, we may, at least in regard to the infra-red or vibrational levels, adopt the same procedure as that which has provided itself

abundantly successful in the field of molecular spectroscopy. As is well known, that procedure consists in determining and enumerating the different possible modes of vibration in each one of which the atoms all vibrate with the same frequency and in the same or opposite phases.

In endeavouring to carry through the procedure indicated above, the difficulty immediately presents itself that the group of atoms present in any one unit cell of the crystal structure is not isolated but forms a connected system with the groups of atoms in the surrounding cells and these latter again are connected with groups of atoms further out and so forth. The mathematical and physical difficulties which present themselves by virtue of these interconnections disappear when we make use of the fundamental property of crystal structure, *viz.*, that it comes into coincidence with itself following a unit translation along any one of its three axes. Hence any normal mode of vibration should also possess the same property, *viz.*, it remains a normal mode following a unit translation of the crystal. This requirement immediately enables us to determine and enumerate the normal modes in the most general case of a crystal consisting of several interpenetrating Bravais lattices of equivalent atoms. It emerges that the normal modes are divisible into two classes; in the first class, the amplitudes as well as the phases of oscillation of equivalent atoms in adjoining cells of the lattice structure are identical, while in the second class of normal modes the amplitudes of equivalent atoms are the same but the phases are reversed along one or two or all three of the axes of the lattice. If the crystal consists of p interpenetrating Bravais lattices, there are $(3p - 3)$ normal modes of the first class and $21p$ modes of the second class.

Thus the result emerges that the vibrational energy levels of a crystal form a sharply defined set in much the same manner as the vibrational energy levels in the spectra of molecules. But this result would necessarily be modified when the effects of anharmonicity and the interactions of the different normal modes with each other are taken into consideration.

6. THE SPECTROSCOPIC BEHAVIOUR OF CRYSTALS

The theoretical results stated above are in complete agreement with the actual spectroscopic behaviour of crystals in the infra-red region of frequencies as revealed by diverse techniques of observation in appropriate physical conditions. For example, they furnish an immediate explanation of the spectroscopic effects exhibited by crystals in the scattering of monochromatic light as mentioned earlier. In some cases the energy levels are shown by the spectral shifts to exhibit a lack of sharpness. That this arises from the disturbing effects of anharmonicity is demonstrated by cooling

down the crystal to liquid air temperature. The energy levels then become perfectly sharp, as is to be expected. We need not dilate here upon the different techniques of spectroscopic observation which are available only in particular cases. Mention should be made, however, of the very general method of observing the energy levels in crystals by the techniques of infra-red absorption. These latter have been greatly improved of recent years and the results obtained with such improved techniques completely confirm the theoretical findings stated above.

A feature of special interest to which reference may be made here is in respect of the possibility of observing the 21 p normal modes of the second class in which the phases of oscillation are opposed in adjoining cells of the crystal structure. It is to be expected that by reason of such opposition of phase these modes would be precluded from observation by any of the available methods of spectroscopic study. Fortunately, however, and for reasons which I shall not here dilate upon, this is not invariably so. The normal modes of the second class are actually accessible to observation in several cases and they then manifest themselves as discrete and sharply defined lines in the spectra, provided the effects of anharmonicity are either absent or else are suppressed by the use of adequately low temperatures. Their appearance is one of the most striking vindications of the correctness of the present theoretical approach.

7. The Specific Heats of Crystals

Regarding a crystal as an assembly of an immense number of oscillators in thermodynamic equilibrium, the evaluation of its thermal energy as a function of the temperature reduces itself to the problem of classifying and enumerating the different sorts of oscillators comprised in it and determining the scheme of energy levels for the oscillators of each sort. An application of Boltzmann's principle then enables us to evaluate the average energy of an oscillator of that sort, and multiplying it by the number of such oscillators we obtain a sum total; the addition of the sums thus found for the different sets of oscillators give the total thermal energy of the crystal. By differentiating this total with respect to the temperature, we obtain the specific heat of the crystal.

As already stated, we have $(3\,p - 3)$ normal modes of vibration of the first kind and 21 p normal modes of the second kind. Thus, we have $(24\,p - 3)$ modes and frequencies in all and these have equal statistical weight. They may be regarded as the internal modes of vibration of the 8 p atoms contained in a volume element of the crystal whose dimensions are twice as large in each direction as the unit cell of the crystal structure. The

three omitted degrees of freedom represented the translatory movements of these groups of $8p$ atoms each. If we leave the latter aside for a moment and also neglect the effects of anharmonicity, the specific heat of a crystal may be expressed very simply as the sum of $(24p - 3)$ Einstein functions, each involving its own characteristic frequency ; the total number of oscillators which contribute is the number of groups of $8p$ atoms each comprised in the crystal. To this sum must be added the contribution to the specific heat arising from the oscillations inside the crystal which are attributable to the translatory movements of these groups of $8p$ atoms each. In a paper which has appeared in the October issue of the *Proceedings* of the Academy, it has been shown how the latter contribution may be rigorously evaluated. The argument by which this is effected may be very simply stated. The translatory movements of the groups of $8p$ atoms each give rise to oscillatory movements in volume elements which comprise a still larger number of atoms. By taking a succession of volume elements of different sizes and taking note of the circumstance that the lower limit of frequencies of vibration thus arising would diminish in proportion to the increasing dimensions of the volume element, the spectral distribution of frequencies follows immediately. Their contribution to the thermal energy of the crystal is found to be expressible as an integral having a well-known form involving Einstein's expression for the average thermal energy of a harmonic oscillator.

It may be mentioned in conclusion that the method sketched above has been successfully applied to the evaluation of the specific heats of crystals—including especially diamond and the metallic elements—down to the very lowest temperatures approaching absolute zero. The theory emerges triumphantly from the test.

8. SUMMARY

The fundamental notions of quantum theory and thermodynamics indicate that a crystal should be regarded as an assembly of an immense number of oscillators whose energy states are quantised and which form a system in thermodynamic equilibrium. They also indicate that the spectroscopic properties and the thermal behaviour of crystals stand in the closest relation to each other. We are thus left with the problem of discovering and enumerating the oscillators of the different sorts comprised in the crystal and of determining their scheme of energy levels. This may be done by methods analogous to those which have proved successful in the field of molecular spectroscopy. The results obtained are in perfect agreement with the observed spectroscopic properties and thermal behaviour of crystals.

Reprinted from "The Proceedings of the Indian Academy of Sciences", Vol. XLIV, No. 6, Sec. A, 1956

THE SPECIFIC HEATS OF CRYSTALS

Part III. Analysis of the Experimental Data

BY SIR C. V. RAMAN

(Memoir No. 91 from the Raman Research Institute, Bangalore-6)

Received November 29, 1956

1. INTRODUCTION

A THEORY of the specific heats of crystals has been put forward in Part I of this series of papers which is based on the determination and enumeration of the normal modes and frequencies of vibration of the atoms in the crystal about their positions of equilibrium. The theory enables the thermal energy of a crystal to be expressed as a function of the temperature in terms of these frequencies. Diamond is admirably suited for a test of the theory, since the frequencies of vibration of the atoms in its structure may be evaluated theoretically and the same frequencies also admit of precise measurement by several different spectroscopic techniques. The specific heat of diamond can accordingly be determined in terms of these frequencies over the whole range of temperatures for which reliable data are available. As has been shown in Part II of this series of papers, the theory emerges triumphantly from the test, its results being in complete accord with the results of the spectroscopic investigations on the one hand and with the measured specific heat data on the other.

In the present memoir we shall consider the converse problem of deducing the nature of the atomic vibration spectrum for a given crystal from the empirically determined specific heat data. The method adopted for this purpose may be briefly stated here. We assume that all the atomic oscillators in the crystal have a common frequency of vibration and calculate from the observed specific heat at any given temperature what that frequency is. The frequency thus evaluated itself appears as a function of the temperature, and a graph showing its variation over the entire range of temperature gives us a useful indication of how the total number of degrees of atomic freedom is distributed over the entire range of frequencies covered by the atomic vibration spectrum of the crystal. The results obtained by this procedure and their significance are best understood by considering an actual example. We shall apply the method to the analysis of the specific heat data for diamond and show how useful conclusions may be derived therefrom.

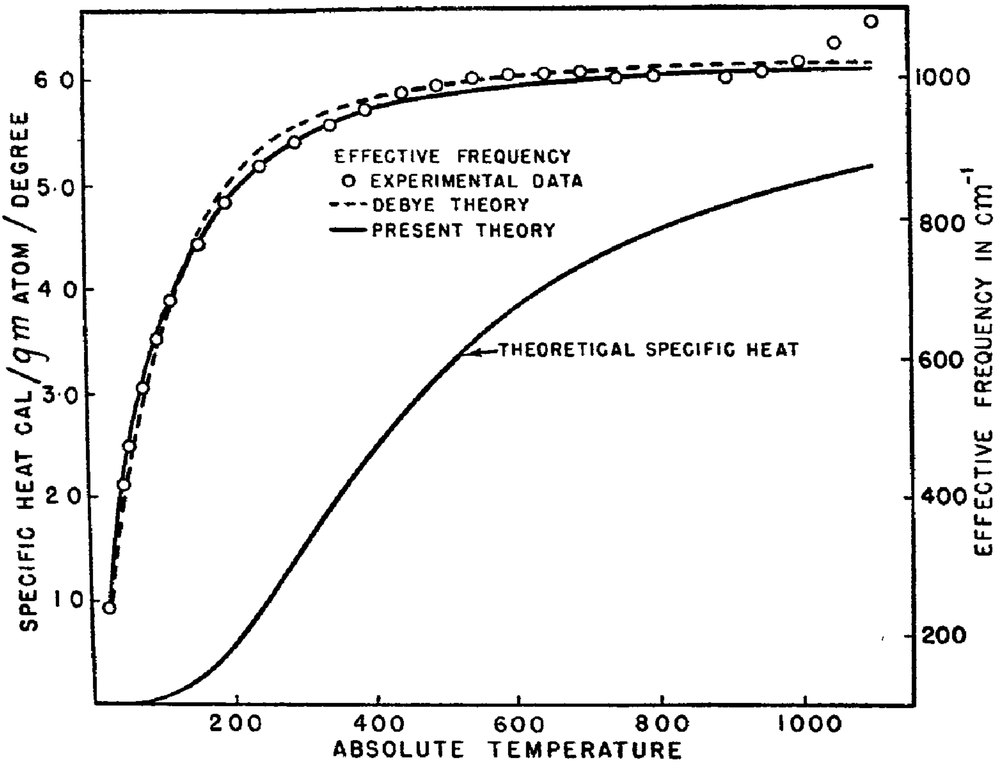

FIG. 1. Analysis of the Specific Heat of Diamond.

2. ANALYSIS OF THE SPECIFIC HEAT CURVE

In Fig. 1 above, we reproduce the graph of the specific heat of diamond as a function of the temperature deduced from the spectroscopic data in Part II of the present series of papers. The abscissæ in the figure are the absolute temperatures, while the ordinates give the calculated specific heats the scale for the same appearing on the left-hand side of the figure. Taking the value of the specific heat given by this graph for any given temperature and with the aid of a table of Einstein's specific heat function, a frequency of vibration is found which, if ascribed to all the atomic oscillators in the crystal, would give that value for the specific heat at that temperature. We may call the frequency thus evaluated the *effective average* of the atomic vibration frequencies at that temperature. A graph showing how this effective frequency varies with the absolute temperature appears in Fig. 1 as a continuous curve; the scale of frequencies is that shown on the right-hand side of the figure. It will be seen that the graph is practically a horizontal line at the highest temperatures, the frequency having the value 1016 cm.$^{-1}$

at 1100°; it then drops very slowly, being 1013 at 1000°, 1006 at 800°, and 992 at 600° K. Thereafter, it falls a little more quickly, being 978 at 500°, 954 at 400°, 911 at 300°, 826 at 200° and 767 at 160°. At still lower temperatures, the frequency drops down steeply and at 25° reaches the value 247 $cm.^{-1}$

The course taken by the frequency-temperature curve is readily understood if we recall the features exhibited by Einstein's specific heat function for various values of the argument; the function vanishes for large values of the argument, while for small values it reaches a limit in the vicinity of which the function does not vary appreciably with the argument; intermediately, however, the function decreases progressively as the argument increases and at an approximately uniform rate. The specific heat curve which we have analysed was obtained by the summation of a set of Einstein functions with different arguments, giving them fractional weights proportionate to the number of oscillators having the particular frequencies. In these circumstances, the " effective average frequency " deduced in the manner explained would necessarily vary with the temperature; at high temperatures, the " *effective average frequency* " would be the same as the *arithmetical average of the frequencies multiplied by their respective weights* but with the very lowest frequencies excluded in casting the average. At moderately high temperatures, the effective average would continue to approximate to the arithmetical average, but if the temperature be so low that the Einstein functions for some of the higher frequencies become vanishingly small, it would show a marked fall and finally, when all the higher frequencies have dropped out in the summation, it is the few surviving oscillators with the lowest frequencies that would determine the effective average frequency. The latter would then be necessarily very small.

The specific heat curve appearing in Fig. 1 was derived from a set of Einstein functions representing monochromatic frequencies whose values and respective degeneracies are the following: 1332 (3), 1250 (8), 1239 (6), 1149 (4), 1088 (6), 1008 (4), 740 (6) and 621 (8) and, in addition, a residual continuous spectrum with a weight three. The arithmetical sum of all these vibration frequencies multiplied by their respective degeneracies and divided by the total of 48 is 987 $cm.^{-1}$ If, however, we omit the continuous spectrum and take the arithmetical average after division by 45, we obtain 1022 $cm.^{-1}$ as the arithmetical average frequency. This is nearly the same as the value of the effective average frequency at 1100° which is 1016 $cm.^{-1}$ The course of the graph in the middle ranges of temperature is determined by the relative weights of the different frequencies. It will be noticed that these weights are distributed in a more or less uniform manner over the entire range from

1332 cm.$^{-1}$ to 621 cm.$^{-1}$ It is this feature which is responsible for the graph of the effective frequency dropping quite gradually from 978 cm.$^{-1}$ to 767 cm.$^{-1}$ in the temperature range between 500° and 160°.

3. Comparison with the Observations

As has already been shown in Part II of this series of papers, a highly satisfactory agreement emerges when the specific heat computed from the spectroscopic data is compared with the values measured by DeSorbo in the temperature range from 40° to 300° and by Magnus and Hodler between 300° K. and 1100° K. The same comparison may be made in a different manner, *viz.*, by calculating from the observed specific heat at any temperature the effective average of the frequencies of the atomic oscillators and plotting them on the same graph as the effective average calculated from the theoretical specific heat curve. This has been done and the experimental values are shown as circles in Fig. 1 above. The specific heats from 40° to 300° were in the present instance taken from the table of smoothed means given by DeSorbo as best representing his determinations [*Jour. Chem. Phys.*, **21** (1953), 876]. The experimental data from 300° upwards were those determined by Magnus and Hodler [*Annalen der Physik.*, **80** (1926), 808]. It will be seen that over the whole range of temperatures upto 400° the experimental values fall smoothly on the theoretical curve. Between 400° and 1000° the experimental values lie about the theoretical curve, but there are appreciable deviations of about $\pm$ 10 cm.$^{-1}$ In this region of temperatures, this would correspond to variation in the specific heats of about 2 per cent. of the measured values. These differences may be reasonably explained as due to inevitable errors in the determination of the specific heats at such high temperatures with small quantities of the material (10 grams).

4. Analysis of Debye's Specific Heat Function

The values for the specific heat of diamond given by Debye's theory have been analysed in the same manner as that explained above and represented in Fig. 1 as a broken line. In making this calculation, the upper limit of frequency in the Debye integral has been taken to be 1332 cm.$^{-1}$ which is the spectroscopically observed highest fundamental frequency. This limiting frequency also fits the experimentally observed specific heats between 450° and 1100° with an accuracy of 1 per cent., the deviations being as often positive as negative. It should also be remarked that the limiting frequency calculated from the elastic constants of diamond comes out as 1304 cm.$^{-1}$ in fair agreement with the spectroscopic value of 1332 cm.$^{-1}$

Comparing now the continuous curve and the broken line appearing in Fig. 1, it will be seen that the latter lies entirely above the former in the

temperature range from 1100° to 140°. The broken curve crosses the continuous curve at about 140° and lies below the latter down to the lowest temperatures.

This difference in the course of the two curves is highly significant. For, it indicates that between 140° and 400°, the Debye theory gives consistently lower specific heats than those actually observed, while between 40° and 140°, it gives higher specific heats than those observed. The actual specific heats, theoretical as well as those observed in these ranges, have been plotted in Figs. 2 and 3 below, as continuous and broken curves and as circles respectively, and exhibit this situation very clearly.

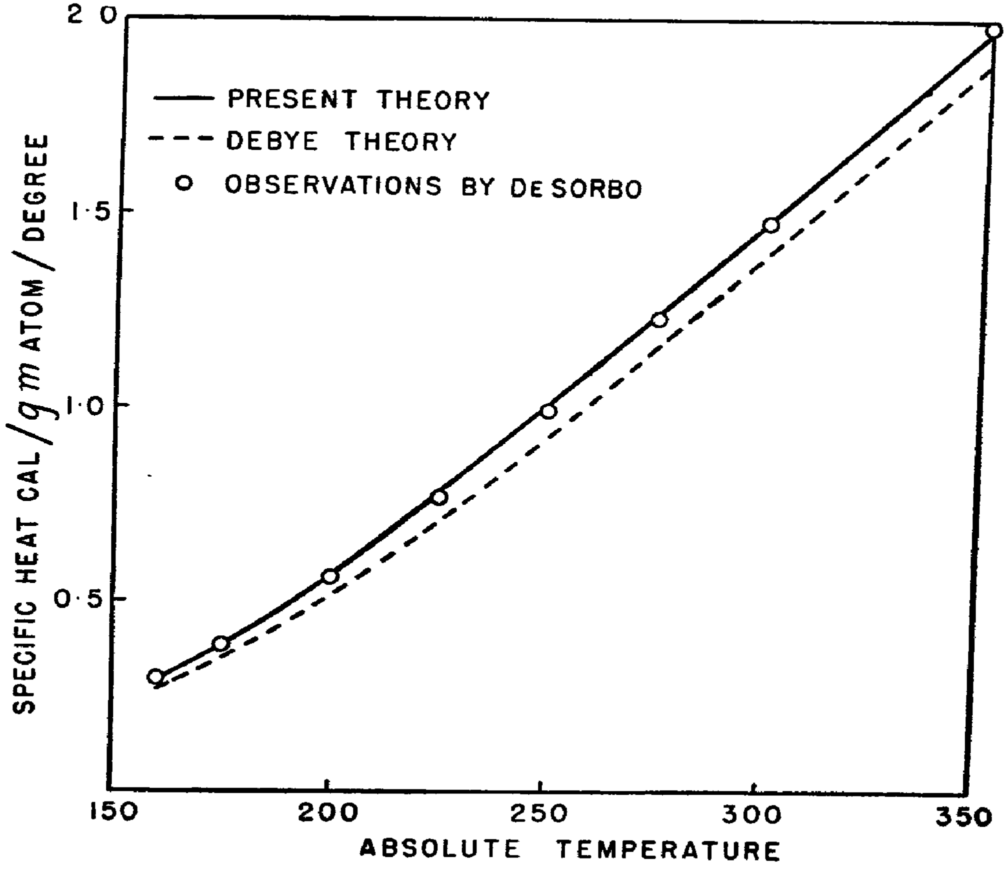

FIG. 2. Specific Heats of Diamond.

5. Comments on Debye's Theory

We shall now consider the theoretical implications which attach to the facts elicited by the foregoing analysis.

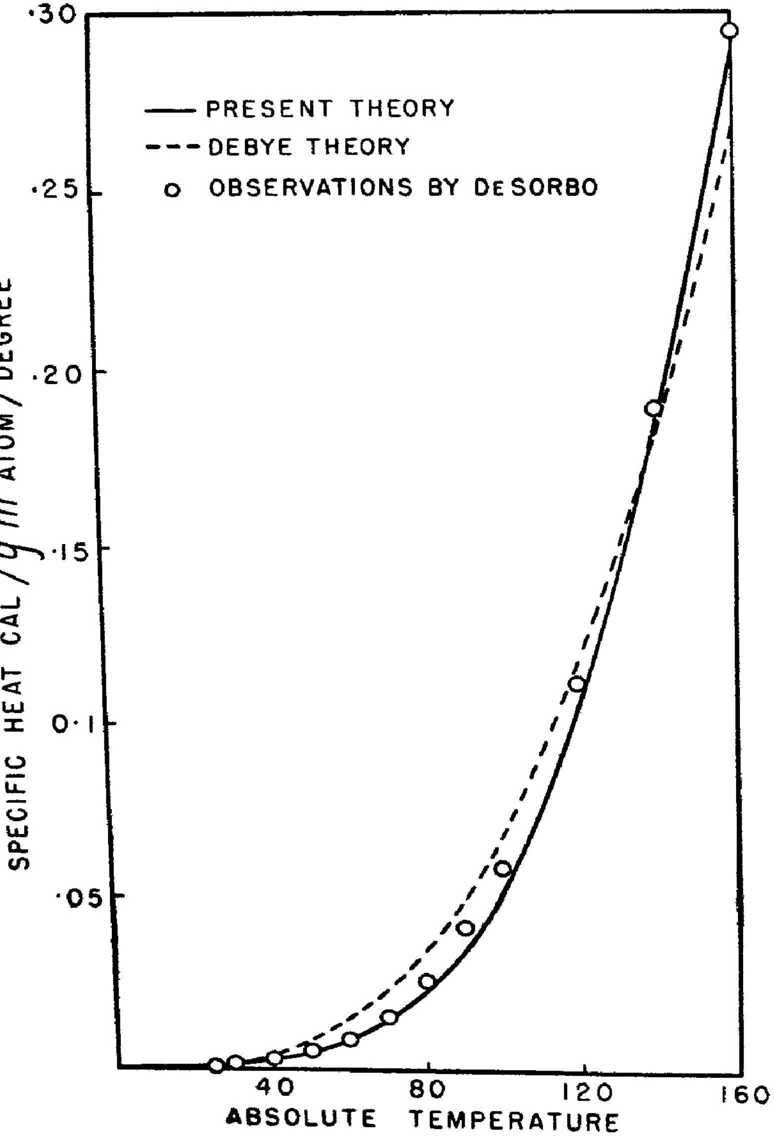

Fig. 3. Specific Heats of Diamond.

In the first place we remark that since the effective average frequency in the temperature range between 1100° and 500° lies close to 1000 cm.$^{-1}$, any assumption whatever regarding the distribution of frequencies in the atomic vibration spectrum which gives us 1000 cm.$^{-1}$ as the effective average would fit the specific heat data satisfactorily within the limits of error of the experimental determinations. If, for example, we assume that all the atomic oscillators had a frequency of 1000 cm.$^{-1}$, the calculated specific heat would agree with the observed values in that temperature range within one or two per cent. Likewise, if we assume that half the atomic oscillators have a frequency of 1332 cm.$^{-1}$ and the other half have the frequency 666 cm.$^{-1}$ thereby giving us an average frequency of 999 cm.$^{-1}$, the specific heat data would also be fitted in that range with the same measure of accuracy. It follows that the agreement between the specific heat theory of Debye and the experimental determinations in this temperature range only indicates that the distribution of frequencies assumed in that theory gives the arithmetical average of the frequencies more or less correctly. That is so, since the arithmetical average is three-fourths of the limiting frequency and is therefore 999 cm.$^{-1}$

The second remark we have to make is that the precise course of the specific heat curve in the middle range of temperatures, in other words, between 140° and 500°, is of the highest importance in enabling us to decide whether or not any assumed distribution of frequencies agrees with or differs radically from the actual distribution. It has already been remarked that in this range the Debye function gives systematically a lower specific heat than that observed, the maximum deviation expressed as a percentage being about 10 per cent. at about 200° K. The present analysis makes it clear that this difference arises because the distribution of the frequencies contemplated in the Debye theory differs radically from the actual distribution; instead of all the frequencies being densely crowded together near the upper end of the frequency range, they are actually distributed in a more or less uniform manner over a wide range of frequencies. It may be remarked that a deviation in the opposite sense, *viz.*, with the calculated values higher than the observed ones, appears in the same temperature range if we assume that half the oscillators have a frequency of 1332 cm.$^{-1}$ and the other half a frequency of 666 cm.$^{-1}$ This makes it clear that the actual distribution of frequencies does not involve a division of the atomic oscillators into two groups with such widely separated frequencies.

The third and the final remark that we have to make is in respect of the specific heats of diamond in the lowest part of the temperature range. The

failure of the Debye theory to represent the course of the specific heat curve in this region is very conspicuous. A great many measurements were made by DeSorbo in this part of the temperature range and as he himself has pointed out, they deviate markedly from the course of the Debye function based on a constant limiting frequency. DeSorbo has exhibited this failure by drawing a graph representing the " characteristic Debye temperature " as a function of the temperature, and this exhibits a pronounced peak at 60°. As will be seen from our Fig. 3, the specific heat at this temperature given by the Debye theory assuming the limiting frequency to be 1332 cm.$^{-1}$ is 60 per cent. in excess of the observed value.

Debye claimed in his original paper that the explanation of the behaviour of the specific heat of crystals at the lowest temperatures constituted the major success of his theory. Since, as we have seen, the theory actually fails most completely at these same low temperatures in the case of diamond, the only possible inference which can be drawn from the facts is that the identification of the thermal energy of crystals with the energy of stationary elastic vibrations in their interior on which the theory is based is a misconceived idea, in other words, that the theory itself is fundamentally untenable.

6. SUMMARY

The functional dependence of the specific heat of a crystal on the temperature may with advantage be expressed as a variation with temperature of the effective average frequency of the atomic oscillators, the same being determined from the argument of the Einstein function which gives the observed specific heat at that temperature. The usefulness of this representation is shown in the paper by a detailed discussion of the experimental data for diamond. It emerges that the distribution of frequencies adopted in the Debye theory is irreconcilable with the observed course of the frequency-temperature curve. It is also pointed out that the large excess which the specific heat calculated from that theory exhibits over the observed values in the region of low temperatures shows that the ideas on which that theory is based are misconceived and that the theory itself is untenable.

Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XLIV, No. 6 Sec. A, 1956

GENERALIZED THEORY OF INTERFERENCE AND ITS APPLICATIONS

Part II. Partially Coherent Pencils

BY S. PANCHARATNAM

(*Memoir No.* 92 *of the Raman Research Institute, Bangalore*-6)

Received November 17, 1956

(Communicated by Sir C. V. Raman)

§ 1. INTRODUCTION

Two beams in different states of polarisation are said to be incoherent when they cannot be made to interfere even after being resolved into the same state of vibration by the use of an analyser. Thus, if unpolarised light be incident on a transparent wedge of quartz the fact that the two oppositely polarised beams into which it is split are incoherent is experimentally demonstrated by the complete absence of interference effects using an analyser alone. Similarly we can speak of two polarised beams as being completely coherent only when, by the use of a suitable analyser, interference effects of maximum clarity can be produced—the interference minimum having zero intensity.

As was remarked in Part I (Pancharatnam, 1956) if an extended source of light be viewed through a plate of an absorbing biaxial crystal cut normal to an optic axis, faint interference rings can be seen by the use of an analyser alone behind the crystal plate—even with the incident light unpolarised. It follows that when a pencil of unpolarised light falls on such a medium, the two non-orthogonally polarised pencils into which it is split must be regarded as partially coherent—since they satisfy neither the test for incoherence nor that for coherence, given in the previous paragraph. Hence, a discussion of the interference phenomena presented with an analyser alone involves really the analysis of the interference of two partially coherent beams which are resolved to the same state of elliptic vibration by the use of an analyser (§ 4). Even when both polariser and analyser are absent, rudimentary traces of an interference pattern may be seen. This requires the analysis of the following problems: the direct interference of two partially coherent beams in different states of polarisation (§ 6); the composition of two such partially coherent beams to form a partially polarised beam—at the second face of the crystal (§ 6); and the converse process—occurring at the first face of the plate—of decomposing unpolarised light (or, more generally, incompletely

polarised light) into two completely polarised vibrations which, we shall find, are partially coherent (§ 7). In § 8 we shall consider the addition of n partially coherent beams which are all completely polarised.

We may mention that without resort to the use of absorbing biaxial crystals, it is easily possible to produce two partially coherent polarised beams. For example, we will have two such completely polarised and physically separate pencils of light emerging from a rhomb of calcite if we allow a single narrow pencil of *partially* polarised light to fall on the first face. The test of their partial coherence is as before the fact that even after being resolved into the same state of vibration by the use of an analyser, their interference is only partial—as may be seen in a conoscopic arrangement. [Our study of such partially coherent beams in opposite states of polarisation (§ 5) has an interesting theoretical consequence: it reveals in a direct manner the equivalence of the Poincaré and the Stokes representation of an arbitrarily polarised light beam.]

The mutual interference characteristics of two incompletely coherent polarised beams which have been derived by the splitting of an incompletely polarised beam can no doubt be described using only the extreme concepts of coherence and incoherence. For example, at the end of § 7 we shall show that when unpolarised light is split into two non-orthogonally polarised elliptic vibrations, the partially coherent components obtained will behave as if a certain independent fraction f of the intensity of one beam were completely coherent with the whole of the second beam—having a definite phase advance over it; this result is obtained by regarding the original unpolarised beam as the sum of two incoherent beams in *specific* orthogonally polarised states. Similarly, if we consider the example of partial coherence quoted in the previous paragraph, the partially polarised pencil (falling on the calcite rhomb) may be regarded as composed of a polarised and an unpolarised portion which are incoherent: the calcite splits the former into two *coherent* and the latter into two incoherent orthogonal vibrations. Thus, the two orthogonally polarised pencils emerging from the calcite will behave as if an independent fraction f_1 of one pencil were completely coherent with an independent fraction f_2 of the second (having a definite phase advance over it), the remaining fractions being incoherent with one another. An unsatisfactory feature of such methods of analysis is that the result depends essentially on regarding the given incompletely polarised beam as the sum of two other incoherent beams (whose decomposition characteristics are known in terms of the ideas of coherence and incoherence alone). For example, we would have arrived at a completely different picture of the state

of affairs existing between the partially coherent pencils emerging from the calcite rhomb, if we had regarded the incident partially polarised beam as the sum of two incoherent orthogonally polarised pencils of different intensity. A second unsatisfactory feature is that though we may be sure that these different pictures of the same state of affairs must lead to identical results, the reason why in fact they do so—*i.e.*, the invariant character underlying these and other possible representations of two partially coherent beams —becomes veiled in obscurity.

In order to effect a deeper analysis of the problem it becomes necessary to have (*a*) a method of defining directly the state of partial polarisation of any beam—without having to regard it as the sum of two other beams; and (*b*) a method of defining directly the mutual parameters (the degree of coherence and the effective phase difference) which will determine the consequence of the superposition of any two polarised beams—without having to regard each beam as the sum of several independent fractions. These two problems will accordingly be discussed in the two subsequent articles.

§ 2. THE REPRESENTATION OF PARTIALLY POLARISED LIGHT

Since, as has already been remarked, the addition of two partially coherent beams in different states of elliptic polarisation results in a beam which is necessarily incompletely polarised, we shall in this section digress on a method of extending the Poincaré method so that it may also be used to represent the state of a partially polarised beam. This extension (and its relation to the representation introduced by Stokes) has already been indicated by Fano (1949) and discussed in more detail by Ramachandran (1952) —but we shall introduce it in a somewhat different fashion which is more suited to our present requirement. The present section also constitutes in itself a presentation of the subject of the Stokes parameters of partially polarised radiation by a new procedure—through the Poincaré representation itself. The conventional presentation of the subject of Stokes parameters may be found in Chandrasekhar (1949) and Rayleigh (1902).

Hitherto (see Fig. 1) we have represented the state of polarisation of an elliptic vibration by a corresponding point P on a Poincaré sphere of unit radius whose centre is O. (The longitude 2λ gives the azimuth λ of the major axis, and the latitude 2ω gives the ellipticity $\tan\omega$.) Instead, if we draw in the direction OP a vector **s** whose length s is made equal to the intensity i of the elliptic vibration, then this vector represents not only the state of polarisation but also the intensity of the elliptic vibration. We

shall refer to **s** as the '*Stokes vector*' defining the *ideal* elliptic vibration (see next paragraph).

We shall now describe in an explicit manner the picture—assumed implicitly in the usual presentation of Stokes parameters—of the vibration in an *actual* beam of sensibly monochromatic radiation. It is known that the existence of incompletely polarised beams and of beams not coherent with one another can be reconciled with the wave theory of light when the extremely short period of light vibrations is taken into account. The phenomena depending on the interference of light merely show that for a duration very long compared with the period of the light wave, the vibration of the light cannot depart sensibly from an ideal periodic vibration described in two dimensions—*i.e.*, an elliptic vibration constant in form, intensity and absolute phase. During this interval the vibration can be characterised by a definite temporary 'Stokes vector' **s**. In a light beam of the most general type we can conceive, with constant macroscopic properties, the vector **s** which specifies the temporary intensity and polarisation may yet fluctuate millions of times a second. The optical characteristics of the beam observed in usual experiments depend only on certain average quantities. These, we find, are the intensity I (which is the average of the temporary intensity *i*) and a vector **S** which is the average of the temporary 'Stokes vector' **s**. Thus

$$\mathrm{I} = \langle i \rangle ; \; \mathbf{S} = \langle \mathbf{s} \rangle \tag{1}$$

where the bent brackets denote 'the average value of'. The vector **S** may be called the three-component part of the Stokes vector of the actual light beam, but we shall merely refer to it as the Stokes vector. The Stokes vector may be specified by its components with respect to any co-ordinate system with origin at the centre of the sphere. In the particular case when we choose a right-handed co-ordinate system $OX_0Y_0Z_0$ with the X_0Y_0 plane coinciding with the equatorial plane, the components of **S** will be denoted by Q, U, V. The four quantities I, Q, U, V will be called the Stokes parameters of the beam (with reference to co-ordinate axes on the wave-front of the beam given by X_0 and X_0'). In presenting the subject in this fashion we are anticipating the fact (to be proved in § 5) that the parameters defined in this geometrical manner in the Poincaré representation are identical with those introduced by Stokes analytically in an entirely different manner.

In the special case of a completely polarised beam there are no fluctuations in the temporary polarisation but only in the temporary intensity *i*;

hence the temporary Stokes vector **s** does not fluctuate in direction but only in its length i. In this case we have obviously I = S, or

$$I = Q^2 + U^2 + V^2 \tag{2 a}$$

When there are *also fluctuations in the temporary polarisation* (*i.e.*, in the direction of s) the beam is partially polarised (or, in special cases, unpolarised). In such cases the specification of the intensity I in addition to the Stokes vector **S** is no longer redundant. If f_j denotes the fraction of the time for which the vibration is in the state $\mathbf{s}_j$ then the Stokes vector **S** is by definition the sum of the vectors $f_j\mathbf{s}_j$. Now it is an obvious geometrical fact that the resultant of a number of vectors not all in the same line must have a length S which is less than the sum of the lengths $f_j i_j$ of the individual vectors. Hence for any beam not completely polarised, I > S or

$$I > Q^2 + U^2 + V^2 \tag{2 b}$$

One may compare the simplicity of the above proof with that used in the usual treatment of Stokes parameters (Chandrasekhar, Rayleigh, *loc. cit.*).

We shall now show that I and **S** together completely determine the appearance presented when the beam is passed through any transparent double refracting crystal followed by a linear analyser—*i.e.*, when the beam is passed through *any* elliptic analyser which transmits completely light of some particular polarisation C (see Part I, § 8). The state of polarisation transmitted by the analyser, instead of being specified by the point C on the Poincare sphere may equally well be specified by a unit vector **C** drawn from the centre of the sphere to the point C. The **C**-component of the beam will then have a temporary intensity i_C which, according to a fundamental property of the Poincaré sphere, is equal to $i \cos^2 \frac{1}{2}\theta$, where θ is the angle between **C** and **s** (see Part I, § 2). Since $i = s$, we have

$$i_C = \tfrac{1}{2}(i + \mathbf{C}\cdot\mathbf{s})$$

where **s** is the temporary Stokes vector of length equal to the temporary intensity i of the beam. The intensity transmitted by an analyser **C** is obtained by averaging as:

$$I_C = \tfrac{1}{2}(I + \mathbf{C}.\mathbf{S}) \tag{3}$$

and is hence determined by I and **S**. This expression will also be of use later.

For unpolarised light we should expect [from our definition of the Stokes vector in (1)] that the Stokes vector should become a zero vector

coinciding with the centre of the sphere. From (3) we see that this is necessarily so since unpolarised light has the property that *any* elliptic analyser C transmits always half the intensity of the beam. (See also Hurwitz, 1945.)

One of the most important properties of the Stokes parameters is the following. *When a number of incoherent beams are mixed, the Stokes vector* **S** *of the resultant beam is the vectorial sum of the individual Stokes vectors* $\mathbf{S}_j$ *of the separate beams* (the intensity I of the resultant beam being naturally the sum of the individual intensities I_j). This readily follows from the fact that the total intensity I_C transmitted by any analyser should be the sum of the transmitted portions of the separate beams—this being the experimental test of their incoherence. Or,

$$I_C = \tfrac{1}{2}(\Sigma I_j + \mathbf{C}.\Sigma \mathbf{S}_j)$$

Since I_C is also given by (3) the required result is obtained. We may also express the result by the statement that when a number of incoherent beams are combined, each Stokes parameter of the resultant beam is the sum of the corresponding Stokes parameters of the individual beams.

A particular consequence of the above result is that any partially polarised beam (I, **S**) may be looked upon as an incoherent combination of a completely polarised beam (S, **S**) and an unpolarised beam (I–S, O). This gives a second physical interpretation of the Stokes vector **S** of a partially polarised beam: *it is a vector whose length is equal to the intensity of the polarised portion of the beam, and whose orientation* (*i.e.*, point of intersection with the Poincare sphere) *gives the state of polarisation of this polarised portion.*

We shall not require any further properties of the Stokes representation than have been derived above.

§ 3. The Degree of Coherence and the Effective Phase Difference Between Two Polarised Beams

We have already noted that in any beam which (for practical purposes) is completely polarised and monochromatic, the form of the elliptic vibration remains constant in time but the temporary intensity fluctuates. In order to explain the fact that it is possible for two polarised beams to be completely incoherent with one another, we must also add that the absolute phase of the elliptic vibration though remaining sensibly constant over successive durations very long compared with the period of light, also fluctuates very rapidly from a macroscopic standpoint (Stokes, 1852). Thus, any two beams

of polarisation A and B travelling along the same direction may be characterised not only by temporary intensities i_1 and i_2, but also by the temporary phase advance δ_t which the vibration in one beam A has over that in the other. The phase difference between two ideal elliptic vibrations not in the same state of polarisation has already been defined in Part I, §§ 3 and 7. (The two vibrations are said to have zero phase difference, when the state of polarisation C obtained by their composition is represented by a point which lies on the great circular arc joining the points representing the states A and B on the Poincare sphere; for oppositely polarised vibrations a special arc AYB is chosen as the great circular arc of zero phase.)

We shall find that the observable characteristics (I, S) of the beam obtained on compounding the two beams depend on the following average quantities correlating the fluctuations in the two beams. These may be called the effective phase advance δ of one beam A over the other, and their mutual degree of coherence γ (defined to be a positive quantity). These are defined—in the same manner as is done in ordinary diffraction theory (Zernike, 1938), where a *scalar* wave theory of light is used—by the relation:

$$\langle \sqrt{i_1 i_2}\, e^{i\delta_t} \rangle = \sqrt{\mathrm{I}_1\, \mathrm{I}_2}\, \gamma\, e^{i\delta} \tag{4}$$

where the sharp brackets are used to indicate the average value. The above relation (in which i represents $\sqrt{-1}$) is equivalent to the two relations

$$2\sqrt{\mathrm{I}_1\mathrm{I}_2}\,\gamma \cos\delta = 2\langle \sqrt{i_1 i_2}\cos\delta_t \rangle = \mathrm{U}', \text{ say}, \tag{5}$$

$$2\sqrt{\mathrm{I}_1\mathrm{I}_2}\,\gamma \sin\delta = 2\langle \sqrt{i_1 i_2}\sin\delta_t \rangle = \mathrm{V}', \text{ say}, \tag{6}$$

so that

$$\left.\begin{aligned} \gamma &= +\frac{1}{2\sqrt{\mathrm{I}_1\mathrm{I}_2}}\cdot\sqrt{\mathrm{U}'^2+\mathrm{V}'^2} \\ \tan\delta &= \frac{\mathrm{V}'}{\mathrm{U}'} \end{aligned}\right\} \tag{7}$$

From (4) we see that δ has the properties of a phase difference: if the instantaneous phase difference is altered by a constant amount, the effective phase difference alters by the same value; while, if the instantaneous intensities are respectively multiplied by constant factors, the effective phase difference is unaltered.

Regarding the degree of coherence γ (defined to be a positive quantity) it may be shown that it lies between the limits zero and unity. The proof is given in Linfoot (1955); it may also be obtained by representing the momentary 'mutual intensity' $\sqrt{i_1 i_2}\exp i\delta_t$ as a vector in an Argand diagram,

applying the argument used in proving (2 *b*), and using the inequality $\sqrt{I_1 I_2} \geqslant \langle \sqrt{i_1 i_2} \rangle$. The beams will be said to be coherent when $\gamma = 1$, which occurs if there is complete correlation between the fluctuations in the two beams—the temporary phase difference as well as the ratio of the temporary intensities being absolutely constant in time. On the other hand when $\gamma = 0$ the beams will be said to be incoherent.

Instead of γ and δ, we shall sometimes find it more convenient to use the correlation parameters U' and V' defined in (5) and (6); or alternatively a single complex quantity I_{12} which has been termed the mutual intensity (Zernike, 1938).

$$I_{12} = \sqrt{I_1 I_2}\, \gamma\, e^{i\delta} = \tfrac{1}{2}(U' + iV')$$

§ 4. Interference of the Components of Two Partially Coherent Beams Transmitted by an Analyser

It is possible to experimentally determine the degree of coherence γ and the effective phase difference δ between two polarised beams of intensities I_1 and I_2, in states of polarisation A and B respectively. This can be done by observing the interference effects after resolving them to the same state of vibration by the use of an elliptic analyser which transmits light of polarisation C. Representing the states of polarisation A, B and C by corresponding points on the Poincaré sphere (see Part I, Fig. 1), the instantaneous intensity i_C transmitted by an analyser C can be expressed in terms of the sides *a*, *b*, *c* of the spherical triangle ABC, and its area E. According to the results of § 8, VII of Part I of this paper, the instantaneous intensities of the resolved components transmitted by the analyser will be $i_1 \cos^2 \frac{1}{2} b$ and $i_2 \cos^2 \frac{1}{2} a$ respectively, their instantaneous phase difference being $(\delta_t - \frac{1}{2} E)$.

Hence

$$i_C = i_1 \cos^2 \tfrac{1}{2} b + i_2 \cos^2 \tfrac{1}{2} a + 2\sqrt{i_1 i_2} \cos(\delta_t - \tfrac{1}{2} E) \cos \tfrac{1}{2} a \cos \tfrac{1}{2} b$$

(It is to be remembered that this expression holds also in the limiting case when A and B represent orthogonal states of polarisation—see Part I, § 8.) The intensity I_C transmitted by the analyser C is obtained by taking the average of the above expression using (4).

$$I_C = I_1 \cos^2 \tfrac{1}{2} b + I_2 \cos^2 \tfrac{1}{2} a + 2\gamma\sqrt{I_1 I_2} \cos \tfrac{1}{2} a \cos \tfrac{1}{2} b \cos(\delta - \tfrac{1}{2} E) \quad (8)$$

This expression will be of much use later.

If we denote the intensities of the resolved components of the two beams by I_1' and I_2' the above result may be written:

$$I_C = I_1' + I_2' + 2\gamma\sqrt{I_1' I_2'} \cos(\delta - \tfrac{1}{2} E) \quad (8')$$

The interference effects will be most pronounced when the intensities of the resolved components (transmitted by the analyser) are equal in magnitude—this being secured by using any analyser C for which $I_1 \cos^2 \frac{1}{2} b = I_2 \cos^2 \frac{1}{2} a$. Under these conditions it can be easily shown that *the visibility of fringes* (as defined by Michelson) *is equal to the degree of coherence* γ. To experimentally determine δ we choose an analyser C for which the area E is zero, so that the point C lies on the great circular arc of zero phase joining A and B (see Part I, §§ 4 and 7). *The effective phase advance δ of one beam over the other can then be measured by the amount by which its path must be retarded in order that the intensity resulting from the interference of the resolved components becomes a maximum.*

From the expression (8) for the intensity transmitted by an analyser C when two partially coherent polarised beams are incident on it, we may deduce the following theorem.

Suppose a number of independent streams of intensities $a_1, a_2 \ldots . a_n$ all in the state of polarisation A are combined with a number of independent streams of intensities $b_1, b_2 \ldots . b_n$ all in the state of polarisation B. Let γ_j and δ_j denote the degree of coherence and the effective phase relation between the *corresponding* pairs of beams a_j and b_j. Then the degree of coherence and the effective phase advance of the resultant beam of polarisation A over that of polarisation B will be given by

$$\sqrt{I_1 I_2}\, \gamma\, e^{i\delta} = \Sigma \sqrt{a_j b_j}\, \gamma_j\, e^{i\delta_j} \tag{9}$$

The above result follows from the fact that the intensity I_C transmitted by any analyser C given by (8), will also be the sum of the intensities $(I_C)_j$, where $(I_C)_j$ denotes the intensity transmitted due to the pair of beams a_j and b_j—this result being true for any value of E. The result may also be expressed by the statement that *the mutual intensity between the resultant beams is the sum of the mutual intensities of the individual pairs.*

As a particular case of the above theorem we note that if an independent fraction f_1 of the intensity of one beam is completely coherent with an independent fraction f_2 of the intensity of the second, having a phase advance δ over it, the remaining portions of the two beams being incoherent, then δ is also the effective phase advance of the first beam over the second, while $\sqrt{f_1 f_2}$ is their mutual degree of coherence. From the above result we obtain a still simpler method of regarding any two partially coherent beams; *an independent fraction γ^2 of the intensity of one beam may be regarded as coherent with the whole of the second beam, having a phase advance δ over it,*

§ 5. Addition of Two Partially Coherent Beams of Opposite Polarisation

Let i_1 and i_2 be the temporary intensities of two vibrations in the opposite states of polarisation X and X′, and let δ_t be the temporary phase advance of the first vibration over the second (Part I, § 7). Let **s** be the immediate value of the Stokes vector of the resultant vibration obtained, whose state of polarisation is represented by the point P (see Fig. 1).

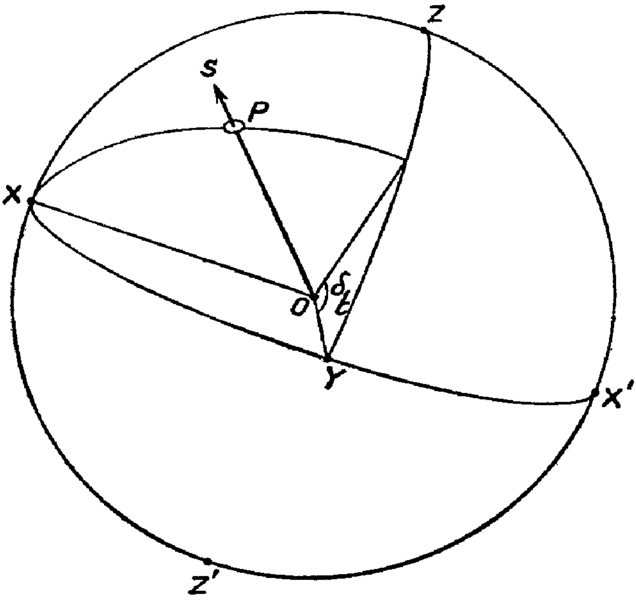

Fig. 1.

P– Momentary state of polarisation of partially polarised beam.

s– Momentary Stokes vector of length equal to the temporary intensity.

δ_t–Instantaneous phase difference between the X and X′ components

We shall refer the temporary Stokes vector **s** to a right-handed system of co-ordinate axes OX, OY, OZ chosen such that the point Y represents the vibration whose X and X′ components are defined to be in the same phase (Part I, § 6). A fundamental property of the Poincare sphere (Part I, § 2, I) is that when a vibration of intensity s in the state of polarisation P is resolved into two oppositely polarised vibrations in the states of polarisation X and X′, the intensities of these components (which are equal to i_1 and i_2) are given by:

$$i_1 = s \cos^2 \tfrac{1}{2}\, \widehat{PX}; \quad i_2 = s \sin^2 \tfrac{1}{2}\, \widehat{PX}$$

or

$$i_1 - i_2 = s \cos \widehat{PX}; \quad 2\sqrt{i_1 i_2} = s \sin \widehat{PX}.$$

But $s \cos \widehat{PX}$ is the projection of the temporary Stokes vector in the OX direction; and $s \sin \widehat{PX}$ is the projection of the temporary Stokes vector on the YZ plane. Now according to Part I, § 6, VI, we have $\widehat{PXY} = \delta_t$. Hence the temporary intensity i and the temporary Stokes vector of the resultant vibration are given by:

$$\left.\begin{array}{ll} i = i_1 + i_2 ; & s_x = (i_1 - i_2) \\ s_y = 2\sqrt{i_1 i_2} \cos \delta_t ; & s_z = 2\sqrt{i_1 i_2} \sin \delta_t \end{array}\right\} \quad (10)$$

We now take the average of the above expressions using (1), (5) and (6). We thus see that *on compounding two oppositely polarised beams of intensities* I_1 *and* I_2 *(for which the mutual degree of coherence and the effective phase advance of the first beam over the second are* γ *and* δ *respectively), the resultant partially polarised beam* (I, S) *is given by*

$$\left.\begin{array}{ll} I = I_1 + I_2 ; & S_x = I_1 - I_2 \\ S_y = 2\gamma\sqrt{I_1 I_2} \cos \delta ; & S_z = 2\gamma\sqrt{I_1 I_2} \sin \delta \end{array}\right\} \quad (11)$$

It may be noted that S_y and S_z are equal to the correlation parameters U′ and V′ respectively.

We shall now consider the converse problem, *viz.*, of resolving a given beam (I, S) into two oppositely polarised beams X and X′—a decomposition which occurs when the beam falls on any transparent crystalline plate. Obviously when the instantaneous vibration **s** of this beam is resolved into vibrations in the states of polarisation X and X′, these component vibrations will have intensities i_1 and i_2, and a phase relation δ_t which satisfy (10). Since the momentary vibration **s** fluctuates for an incompletely polarised beam, it is clear that i_1, i_2 and δ_t will also fluctuate—so that the component beams will, in general, be partially coherent. The intensities I_1 and I_2 of the component beams, their degree of coherence γ and the effective phase advance δ of the first beam over the second can be obtained from (11).

$$\left.\begin{array}{ll} I_1 = \frac{1}{2}(I + S_x) ; & I_2 = \frac{1}{2}(I - S_x) \\ \gamma = +\frac{1}{2\sqrt{I_1 I_2}} \cdot \sqrt{S_y^2 + S_z^2} ; & \tan \delta = \frac{S_z}{S_y} \end{array}\right\} \quad (12)$$

It may be noted that the expression for the effective phase difference δ between the component beams does not involve the degree of polarisation of the given beam,

The first Stokes parameter of a beam is its intensity. We may now easily see that our method of defining the remaining Stokes parameters (as components of the average Stokes vector **S** with respect to a special co-ordinate system) is entirely equivalent to the usual method. To show this we consider the resolution of an arbitrarily polarised beam into two orthogonal *linearly* polarised beams. In this case the states X and X′ in Fig. 1 lie on the equator. The four Stokes parameters of the beam (with respect to axes on the wave-front given by X and X′) are then customarily *defined* as the average values of the expressions on the *right*-hand side of each of the four relations in (10). In our presentation (see § 2), the average values assumed by the quantities i, s_x, s_y, s_z, in the *particular* case when the XY plane of the co-ordinate system lies on the equatorial plane, are the Stokes parameters of the beam (with reference to axes on the wavefront given by X and X′). The relations (10) show that both methods of definition are equivalent. Our method of introducing the Stokes parameters (given in § 2) is more general, in that it does not at all involve the representation of an arbitrarily polarised beam as the sum of two other (partially coherent) linearly polarised beams. In fact such a decomposition is clearly seen to be merely a particular case of the problem which we shall discuss in § 7, *viz.*, the decomposition of any partially polarised beam into two beams in non-orthogonal states of polarisation.

§ 6. Addition of Two Partially Coherent Beams in Non-Orthogonal States of Polarisation

When *any* two beams travelling along the same direction are combined, the instantaneous intensity of the resultant beam is obtained from Part I, § 3, III as

$$i = i_1 + i_2 + 2\sqrt{i_1 i_2}\cos\tfrac{1}{2}c\cos\delta_t$$

where the similarity factor $\cos^2\frac{1}{2}c$ will be absolutely constant in time if the two beams are completely polarised. Averaging the above equation using (5) we obtain the *generalized formula for the interference of two polarised beams of intensities I_1 and I_2, degree of coherence γ and effective phase difference δ:*

$$\mathrm{I} = \mathrm{I}_1 + \mathrm{I}_2 + 2\gamma\sqrt{\mathrm{I}_1\mathrm{I}_2}\cos\tfrac{1}{2}c\cos\delta \qquad (13)$$

Thus γ and δ may be determined by *direct* interference experiments, though the method of using an analyser given in § 4, is to be preferred—to increase the visibility of interference effects. In relation (13), c is the angular separation between the states of polarisation on the Poincaré sphere. The above

relation can also be easily obtained by regarding a fraction γ^2 of the first beam as coherent with the second beam, having a phase advance δ over it.

It remains to find the Stokes vector of the resultant beam. Let the states of polarisation of the two beams be given by the points A and B on the Poincaré sphere, or alternatively by unit vectors **A** and **B** joining the centre of the sphere to the points in question. The Stokes vectors of the two beams are then $\mathbf{S}_1 = I_1\mathbf{A}$ and $\mathbf{S}_2 = I_2\mathbf{B}$. When the beams are not completely coherent it is clear that there will be fluctuations in the temporary state of polarisation and intensity of the resultant vibration—so that the resultant beam will be incompletely polarised. We shall in this section prove that the Stokes vector **S** of the resultant beam may be obtained by the following procedure (see Fig. 2). It is obtained by adding to the sum of the given Stokes vector $\mathbf{S}_1$ and $\mathbf{S}_2$ (directed towards points A and B), a third vector $\mathbf{S}_{12}$ (directed towards a point C″). This last vector which arises because of the interference of the beams, may be specified in terms of the angles of the triangle ABC″ which is isoscles: *the base angles A and B are both equal to the effective phase difference δ between the beams, and the length of vector* $\mathbf{S}_{12}$ *is* $2\gamma\sqrt{I_1 I_2}\sin\frac{1}{2}\hat{C}''$.

The components of the Stokes vector of the resultant beam may be found by using the following proposition which follows from (3): *the component of the Stokes vector along any direction* **C** *is equal to the intensity transmitted by an analyser* **C**, minus *the intensity transmitted by the orthogonal analyser* (— **C**).

i.e.,

$$I_C - I_{-C} = \mathbf{S}.\mathbf{C} \tag{14}$$

Since we have already (in eq. 8) derived the intensity transmitted by any analyser when it is introduced in the path of two partially coherent polarised beams, we may find the Stokes vector **S** of the resultant beam. (It may be remembered that in equation 8, the quantities a, b, c are the sides of the spherical triangle ABC, while E is the area of the triangle—measured with the usual sign convention.) The intensity I_{-C} transmitted by the orthogonal analyser (—**C**) may be obtained from (8) by changing a and b to their supplements, and E to E′, where E′ is the area of the triangle ABC′ columnar to ABC. We then have

$$I_C - I_{-C} = I_1\cos b + I_2\cos a + 2\gamma\sqrt{I_1 I_2} \times \{\cos\tfrac{1}{2}a\cos\tfrac{1}{2}b\cos(\delta - \tfrac{1}{2}E) - \sin\tfrac{1}{2}a\sin\tfrac{1}{2}b\cos(\delta - \tfrac{1}{2}E')\}$$

Since the two beams which are being combined are completely polarised, we have according to (2 a), $I_1 = S_1$ and $I_2 = S_2$, where S_1 and S_2 are the Stokes

vectors of these beams. The first two terms of the above expression are accordingly equal to $\mathbf{S}_1.\mathbf{C}$ and $\mathbf{S}_2.\mathbf{C}$ respectively. Comparing with (14) we see that the Stokes vector $\mathbf{S}$ of the resultant beam may be written as

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_{12} \tag{15}$$

where the term $\mathbf{S}_{12}$ which may be considered as arising from the mutual interference of the beams, may be determined from the relation

$$\mathbf{S}_{12}.\mathbf{C} = 2\gamma \sqrt{\mathrm{I}_1\mathrm{I}_2}\ \{\cos \tfrac{1}{2}\, a \cos \tfrac{1}{2}\, b \cos (\delta - \tfrac{1}{2}\,\mathrm{E}) - \sin \tfrac{1}{2}\, a \sin \tfrac{1}{2}\, b \cos (\delta - \tfrac{1}{2}\,\mathrm{E}')\} \tag{16}$$

It may be noted that $\mathbf{S}_{12}$ is γ times the value which it would have if the beams were completely coherent.

Since the last relation gives the component of $\mathbf{S}_{12}$ along *any* direction C, we may determine the vector $\mathbf{S}_{12}$ by finding its components with respect to the special co-ordinate system OX, OY, OZ given in Fig. 2. The positive x-axis is taken along the direction of the vector $(\mathbf{A} - \mathbf{B})$; the positive y-axis along the direction of the vector $(\mathbf{A} + \mathbf{B})$; and the positive z-axis along the direction of the vector $(\mathbf{A} \times \mathbf{B})$. (The definitions of the y and z directions would have to be slightly modified if we wish also to cover the limiting case, discussed in the previous section, when A and B are oppositely polarised.)

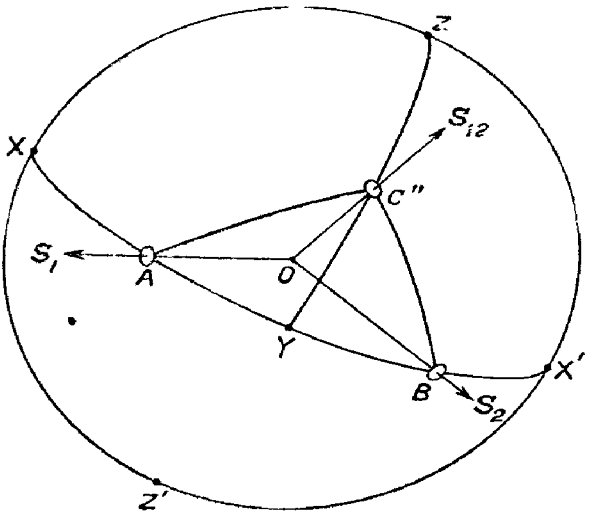

Fig. 2

Composition of non-orthogonally polarised beams S_1 and S_2. The vector for the resultant partially polarised beam is the sum of the three vectors drawn in the Figure; S_{12} has an orientation determined by $A = \hat{B} = \delta$, and a length equal to $2\gamma \sqrt{I_1 I_2} \sin\frac{1}{2}\, \hat{C}''$.

When the unit vector **C** is taken along the x direction (see Fig. 2) we will have in (16), $\cos \frac{1}{2} a \cos \frac{1}{2} b = \sin \frac{1}{2} a \sin \frac{1}{2} b$ and $E = E' = 0$. When the unit vector **C** coincides with the y-axis we have $E = 0, E' = \pi$ and $a = b = \frac{1}{2} c$. Lastly when the direction of **C** coincides with OZ we will have $a = b = \pi/2$ and $E = -E' = c$. Making these substitutions in (16) we obtain the components of $\mathbf{S}_{12}$ as

$$\left.\begin{array}{l}(S_{12})_x = 0 \\ (S_{12})_y = 2\gamma \sqrt{I_1 I_2} \cos \delta; \ (S_{12})_z = 2\gamma \sqrt{I_1 I_2} \sin \delta \sin \tfrac{1}{2} c\end{array}\right\} \qquad (17)$$

We see that the vector $\mathbf{S}_{12}$ lies in the yz plane, and hence that the triangle ABC″ is isoscles. Also the inclination of this vector to the y-axis is equal to the arc YC″ and is given by

$$\tan \widehat{YC''} = S_z/S_y = \tan \delta \sin \tfrac{1}{2} c$$

Since the spherical triangle AYC″ is right angled at Y, it is seen from spherical trigonometry that the above relation implies that the angle at A is equal to δ. This locates the position of C or the orientation of the vector $\mathbf{S}_{12}$. Its length is given by

$$\begin{aligned} S_{12} &= \sqrt{S_y^2 + S_z^2} = 2\gamma \sqrt{I_1 I_2} \cdot \sqrt{(1 - \sin^2 \delta \cos^2 \tfrac{1}{2} c)} \\ &= 2\gamma \sqrt{I_1 I_2} \sin \tfrac{1}{2} C'' \end{aligned}$$

These are the relations for determining the vector $\mathbf{S}_{12}$ which were stated at the beginning of this section, and which we wished to prove. The superposition of oppositely polarised beams, discussed in the previous section, may be considered as a limiting case of the present discussion.

The result may also be expressed concisely in vector notation, the result being then independent of any co-ordinate system. Using the correlation parameters U′ and V′ introduced in (5) and (6) instead of γ and δ, we can then write (17) as

$$\mathbf{S}_{12} = \tfrac{1}{2} \sec \tfrac{1}{2} c \{U' (\mathbf{A} + \mathbf{B}) + V' (\mathbf{A} \times \mathbf{B})\} \qquad (18$$

or

$$\mathbf{S}_{12} = \text{Real part of } I_{12} \mathbf{S}_{12}' \sec \tfrac{1}{2} c \qquad (19)$$

where

$$\mathbf{S}_{12}' = (\mathbf{A} + \mathbf{B}) - i (\mathbf{A} \times \mathbf{B})$$

Hence when two non-orthogonally polarised beams with Stokes vectors $\mathbf{S}_1$ and $\mathbf{S}_2$ are combined, the Stokes vectors **S** of the resultant beam is given by (15) where $\mathbf{S}_{12}$ is given by (18), or (19). The intensity I of the resultant beam is given by (13).

The components of the Stokes vector of the resultant beam (with respect o the special co-ordinate axes chosen) may now be written down from (15) nd (17) by noting that the x-components of S_1 and S_2 will be $I_1 \sin \frac{1}{2} c$ and $- I_2 \sin \frac{1}{2} c$ respectively, while the y-components will be $I_1 \cos \frac{1}{2} c$ and $_2 \cos \frac{1}{2} c$ respectively. Hence the Stokes vector of the resultant beam is ,iven by:

$$\left.\begin{aligned} S_x &= (I_1 - I_2) \sin \tfrac{1}{2} c \\ S_y &= (I_1 + I_2) \cos \tfrac{1}{2} c + 2\gamma \sqrt{I_1 I_2} \cos \delta \\ S_z &= 2\gamma \sqrt{I_1 I_2} \sin \delta \sin \tfrac{1}{2} c \end{aligned}\right\} \tag{20}$$

§ 7. Decomposition of any Beam into Two Non-Orthogonally Polarised Pencils

We now consider a problem which is the converse of that treated in the previous section, *viz.*, the resolution of a given arbitrarily polarised beam (I, **S**) into two non-orthogonally polarised beams in given states of polarisation **A** and **B**. Such a process occurs for example when the beam falls on a plate of an absorbing biaxial crystal.

If **S** denotes the instantaneous Stokes vector of the given beam, then according to the results proved in Part I, § 4, IV, the temporary intensities i_1 and i_2 of the component beams will be given by

$$i_1 = i \frac{\sin^2 \frac{1}{2} \theta_2}{\sin^2 \frac{1}{2} c}; \quad i_2 = i \frac{\sin^2 \frac{1}{2} \theta_1}{\sin^2 \frac{1}{2} c}$$

where θ_1 and θ_2 are the the (momentary) angles that the vector **s** makes with the vectors **A** and **B** respectively.

Now, since $i = s$, this may be re-written thus:

$$i_1 = \tfrac{1}{2} (i - \mathbf{s}.\mathbf{B}) \operatorname{cosec}^2 \tfrac{1}{2} c; \quad i_2 = \tfrac{1}{2} (i - \mathbf{s} \cdot \mathbf{A}) \operatorname{cosec}^2 \tfrac{1}{2} c$$

The average intensities of the non-orthogonally polarised component beams will therefore be

$$I_1 = \tfrac{1}{2} (I - \mathbf{S}.\mathbf{B}) \operatorname{cosec}^2 \tfrac{1}{2} c \; ; \; I_2 = \tfrac{1}{2} (I - \mathbf{S}.\mathbf{A}) \operatorname{cosec}^2 \tfrac{1}{2} c \tag{21}$$

It remains to determine the degree of coherence and the effective phase difference between the component beams, or alternatively the correlation parameters U′ and V′ defined in (5) and (6). The first parameter is obtained by eliminating $(I_1 + I_2)$ from the expression for S_y in (20) by using (13). We thus obtain

$$U' = (S_y - I\cos\tfrac{1}{2}c)\operatorname{cosec}^2\tfrac{1}{2}c \qquad (22\text{-}a)$$

$$= \tfrac{1}{2}\{\mathbf{S}\cdot(\mathbf{A}+\mathbf{B}) - 2I\cos^2\tfrac{1}{2}c\}\operatorname{cosec}^2\tfrac{1}{2}c\sec\tfrac{1}{2}c \qquad (22\text{-}b)$$

The parameter V′ is given by the last relation in (17)

$$V' = S_z\operatorname{cosec}\tfrac{1}{2}c \qquad (23\text{-}a)$$

$$= \tfrac{1}{2}\mathbf{S}\cdot(\mathbf{A}\times\mathbf{B})\operatorname{cosec}^2\tfrac{1}{2}c\sec\tfrac{1}{2}c \qquad (23\text{-}b)$$

or

$$2I_{12} = \tfrac{1}{2}(\mathbf{S}\cdot\mathbf{S}_{21}' - 2I\cos^2\tfrac{1}{2}c\}\operatorname{cosec}^2\tfrac{1}{2}c\sec\tfrac{1}{2}c$$

As a particular example of much interest we may consider the decomposition of *unpolarised* light into two non-orthogonally polarised beams. Since for unpolarised light $\mathbf{S} = 0$, the intensities I_1 and I_2 of the component beams are, according to (21), both equal to $\frac{1}{2}I\operatorname{cosec}^2\frac{1}{2}c$. The effective phase difference and the degree of coherence could be determined by finding the parameters U′ and V′ from (22) and (23). But it is more instructive to go back to relation (15) from which it may be noted that for $\mathbf{S}$ to be a zero vector, $\mathbf{S}_{12}$ must be coplanar with $\mathbf{S}_1$ and $\mathbf{S}_2$. Since $\mathbf{S}_{12}$ must also be in the *yz* plane, it is clear that the point C″ towards which it points must be the mid-point of the greater segment of the great circular arc through A and B. The length of the vector $\mathbf{S}_{12}$ being equal to that of $(\mathbf{S}_1 + \mathbf{S}_2)$ will be given by $(I_1 + I_2)\cos\frac{1}{2}c$. The effective phase difference between the component beams is π (being equal to the angle A of the isosceles triangle ABC″). The degree of coherence between the two beams is $\cos\frac{1}{2}c$ (since the length of the vector $\mathbf{S}_{12}$ is also given by $2\gamma\sqrt{I_1I_2}\sin\pi/2$).

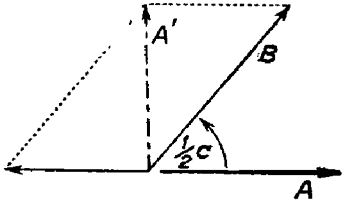

FIG. 3.

Decomposition of unpolarised light into two non-orthogonally polarised beams with vibration-directions along A and B. The resultant beams have a degree of coherence cos ½ c and an effective phase difference of π.

The decomposition of unpolarised light into two non-orthogonal vibrations in the states of polarisation A and B (separated by an angle c on the Poincaré sphere) may be more simply analysed by replacing the unpolarised light by two *incoherent* beams each of intensity $\frac{1}{2}I$ in the ortho-

gonally polarised states A and A′. (In order that the general method may be perfectly clear, the particular case when A and B are linear vibrations inclined at the angle $\frac{1}{2}c$ is drawn in Fig. 3 and may be followed simultaneously.) The beam of polarisation A′ may now be replaced by two coherent beams in the non-orthogonal states of polarisation B and A. These latter two vibrations will have a phase difference of π, since A′ lies on the greater segment of the great circle through A and B (Part I, § 4, V). Their intensities will be respectively $\frac{1}{2}\mathrm{I}\,\mathrm{cosec}^2\,\frac{1}{2}c$ and $\frac{1}{2}\mathrm{I}\cot^2\frac{1}{2}c$ (as is given by the parallelogram law in the case of Fig. 3, and in the general case by substituting $b = \pi$ and $a = \pi - c$ in the results of Part I, § 4, IV). Thus in the state of polarisation B we have a beam of intensity $\frac{1}{2}\mathrm{I}\,\mathrm{cosec}^2\,\frac{1}{2}c$; while in the state of polarisation A we have two incoherent vibrations which add to give a beam of the same intensity $\frac{1}{2}\mathrm{I}\,\mathrm{cosec}^2\,\frac{1}{2}c$. Of the latter beam, however, an independent fraction comprising an intensity $\frac{1}{2}\mathrm{I}\cot^2\frac{1}{2}c$ is completely coherent with the other beam and is opposed in phase to it. In other words, the degree of coherence between the beams is $\cos\frac{1}{2}c$ and the effective phase difference is π (according to the result proved at the end of § 4).

§ 8. The Addition of n Partially Coherent Beams

We shall now consider the addition of n polarised beams whose states of polarisation are represented by the points $P_1.\, P_2 \ldots . P_n$ on the Poincaré sphere, or alternatively by the unit vectors $\mathbf{P}_1.\, \mathbf{P}_2.\, \mathbf{P}_3 \ldots . \mathbf{P}_n$ joining the centre of the sphere to these points. The instantaneous intensity i of the resultant beam will be given by equation (14) of Part I, § 9

$$i = \Sigma\, i_j + \sum_{j \neq k} i_{jk} \cos \tfrac{1}{2} c_{jk}$$

where i_j denotes the temporary intensity of the jth beam, i_{jk} the temporary mutual intensity of the jth beam with respect to the kth and c_{jk} is the angle between the vectors $\mathbf{P}_j$ and $\mathbf{P}_k$. Averaging the above equation we obtain the following expression for the intensity I of the resultant beam:

$$\mathrm{I} = \Sigma\, \mathrm{I}_j + \sum_{j \neq k} \mathrm{I}_{jk} \cos \tfrac{1}{2} c_{jk} \tag{24}$$

where I_{jk} is the mutual intensity of the jth beam with respect to the kth. The second term in (24) arises from the mutual interference of the different pairs of beams.

The form of (24) suggests that the Stokes vector $\mathbf{S}$ of the resultant beam may be obtained by a similar generalisation of relation (15) obtained for two beams:

$$\mathbf{S} = \Sigma\, \mathbf{S}_j + \tfrac{1}{2} \sum_{j \neq k} \mathbf{S}_{jk} \tag{25}$$

or alternatively

$$\left.\begin{aligned} \mathbf{S} &= \Sigma \mathbf{S}_j + \tfrac{1}{2} \Sigma \mathrm{I}_{jk} \cdot \mathbf{S}_{jk}' \sec \tfrac{1}{2} c_{jk} \\ \text{where} \quad \mathbf{S}_{jk}' &= (\mathbf{P}_j + \mathbf{P}_k) - i (\mathbf{P}_j \times \mathbf{P}_k) \end{aligned}\right\} \tag{26}$$

That the relations (25 and 26) do indeed give the Stokes vector of the resultant beam may be verified by taking recourse to the intensity transmitted by any analyser **C** when the n beams are incident on it. This intensity $\mathrm{I_C}$ will be the average of the instantaneous transmitted intensity [which may be obtained by using equation (13) of Part I, § 9]:

$$\mathrm{I_C} = \Sigma \mathrm{I}_j \cos^2 \theta_j + \Sigma \gamma_{jk} \sqrt{\mathrm{I}_j \mathrm{I}_k} \cos \theta_j \cos \theta_k \cos (\delta_{jk} - \tfrac{1}{2} \mathrm{E}_{jk})$$

where $2\theta_j$ denotes the angle between $\mathbf{P}_j$ and **C**, and E_{jk} the area of the spherical triangle $\mathrm{CP}_j\mathrm{P}_k$. The component of the Stokes vector of the resultant beam along any direction C is obtained by writing the value of $(\mathrm{I_C} - \mathrm{L_C})$. Since the $\mathbf{S}_{jk}$ satisfy relations of the type of (16) it may be easily shown that (26) gives the Stokes vector of the resultant beam.

It is a pleasure to acknowledge the encouragement given by Prof. Sir C. V. Raman, F.R.S., N.L., and the keen interest he took in this investigation.

§ 9. SUMMARY

The superposition of two partially coherent but completely polarised beams is discussed. The formula for the intensity of the resultant beam is obtained from the interference formula for coherent beams by multiplying the third interference term by the degree of coherence γ (defined statistically). The states of the two given polarised beams and that of the resultant incompletely polarised beam may be characterised by respective vectors drawn from the centre of the Poincaré sphere: the length of each vector and its orientation (*i.e.*, point of intersection with the sphere) may be regarded as giving respectively the intensity and state of polarisation, of the polarised fraction of the corresponding beam. The vector for the resultant beam is obtained by adding to the sum of the two given vectors (which are directed towards points A and B), a third vector directed towards a point C″ on the Poincaré sphere. This last vector which arises because of the interference of the beams, is specified in terms of the angles of the triangle ABC″, which is isosceles: the base angles A and B are both equal to the effective phase difference δ and the length of the vector is equal to $2\gamma\sqrt{\mathrm{I_1 I_2}} \sin \frac{1}{2} \hat{\mathrm{C}}''$.

The converse problem is discussed and also the addition of n partially coherent polarised beams. The paper also presents the subject of the Stokes

parameters of partially polarised radiation through an extension of the Poincaré representation.

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Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XLV, No. 2, Sec. A, 1957

THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS

Part I. Analysis of the Experimental Data

BY SIR C. V. RAMAN

(*Memoir No.* 93 *from the Raman Research Institute, Bangalore*-6)

Received December 21, 1956

1. INTRODUCTION

IT is proposed in this paper to analyze the data for the variation of the specific heat with temperature of some metallic elements. The method of analysis is that already explained and discussed in an earlier paper[1] in these *Proceedings* with reference to the specific heat data for diamond, *viz.*, to determine, with the aid of a table of Einstein's specific heat function, the particular frequency of vibration which if assumed to be common to all the atomic oscillators would give for the specific heat of the substance the actual value observed at any given temperature. The frequency thus calculated is designated as the effective average frequency of the atomic oscillators for that substance at that particular temperature. It is itself a function of the temperature and a graph showing how it varies as we proceed from the highest to the lowest temperatures gives useful indications regarding the distribution of the atomic degrees of freedom of motion over the entire range of frequencies in the vibration spectrum.

The four metallic elements the data for which will be analyzed in this paper are aluminium, copper, silver and lead. They all crystallize in the cubic system in forms based on the so-called face-centred cubic lattice which is really a simple Bravais lattice with only one set of equivalent atoms occupying the corners of a rhombohedral unit cell. We shall make use of the data for the specific heats of these metals determined by Giaque and collaborators.[2] The four metals form a sequence in which the fall of the specific heat at constant volume from the maximum given by the Dulong-Petit formula manifests itself progressively at lower and lower temperatures. There is a special appropriateness in their choice for the present study, since it was the data for these four metals as well as the data for diamond determined by Nernst and Lindmann[3] which were made use of by Debye[4] in a well-known paper as support for his theory of the specific heats of crystals.

2. THE SPECIFIC HEAT DATA

The specific heat data we make use of are plotted as the lower of the two graphs appearing in Figs. 1, 2, 3 and 4 which refer respectively to the four metals aluminium, copper, silver and lead. The absolute temperatures are entered on the scale of abscissæ at the foot of each figure. The scale of ordinates for the specific heats in cal./gm. atom/degree appears on the left-hand side of each figure. The specific heats observed are shown as dotted circles and fall on a smooth curve which touches the axis of abscissæ at the lowest temperatures and tends to approach the maximum limit at higher temperatures. The scale of ordinates used for the specific heats is rather too small for the values at the very lowest to be adequately represented. The slope of the specific heat curve at the upper end of the temperature range is greatest for aluminium, less for copper, still less for silver, while for lead it is almost indistinguishable from a horizontal straight line.

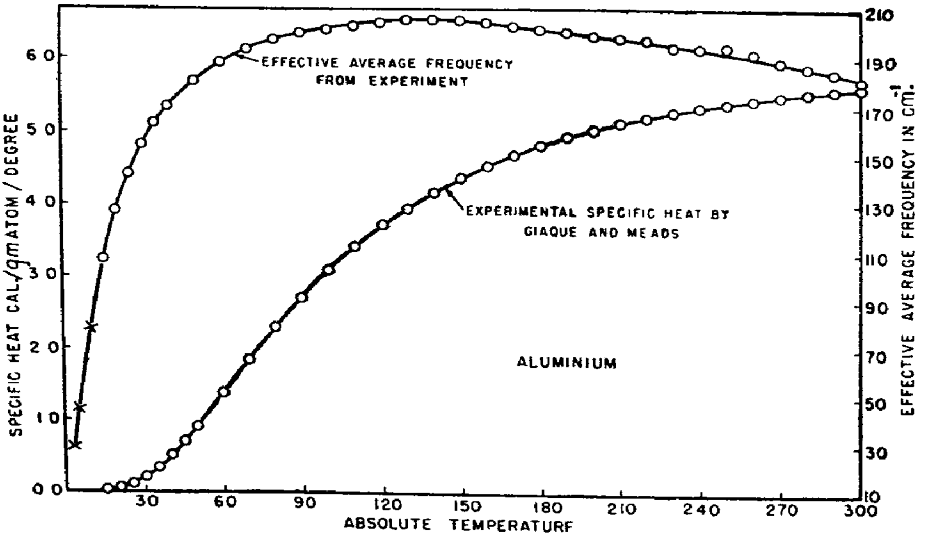

FIG. 1. Analysis of the Specific Heat of Aluminium.

3. THE EFFECTIVE AVERAGE FREQUENCY

The upper of the two graphs in each of the four figures represents the average effective frequency of the atomic oscillators calculated in the manner already explained. The frequencies are shown in the usual spectroscopic nomenclature as wave-numbers and the scale of ordinates for the same appears on the right-hand side of each figure. The calculated values are shown as dotted circles and a smooth curve has been drawn through them. It will

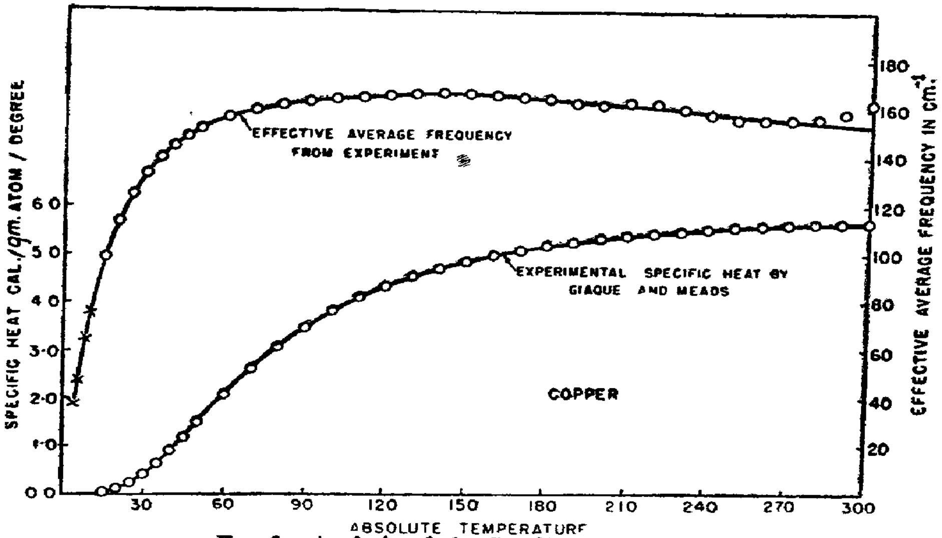

Fig. 2. Analysis of the Specific Heat of Copper.

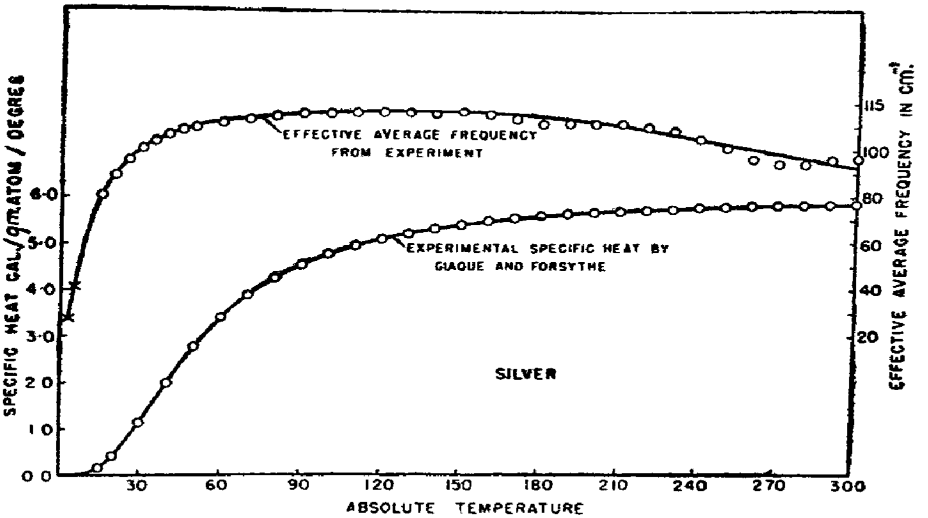

Fig. 3. Analysis of the Specific Heat of Silver.

be seen that they exhibit a certain amount of scatter in the higher parts of the temperature range in each case. This is not surprising, since a very small error in the determination of the specific heat at this part of the range would represent a large error in the calculation of the effective average frequency.

The graphs have been drawn as smooth curves to represent the general trend of the calculated values, ignoring the accidental fluctuations.

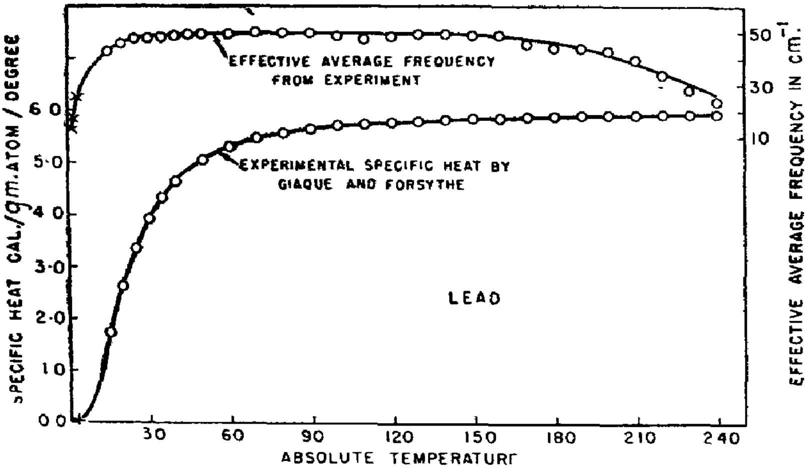

FIG. 4. Analysis of the Specific Heat of Lead.

It appeared important to continue the graphs to still lower temperatures than those covered by determinations by Giaque and collaborators. Accordingly, we have made use of the data obtained by other authors[5–7] for determining the effective average frequency of the atomic oscillators in this lowest part of the temperature range. The computed frequencies are shown as crosses on the extreme left-hand side of the figure in each case and the graphs have been prolonged so as to pass smoothly through those points.

4. THE SIGNIFICANCE OF THE RESULTS

On a comparison of the frequency-temperature graphs for the four metals, it will be seen at once that while there are certain general similarities, there is also a progressive change in form as we go down the series. All the four curves show a maximum in the middle part of the temperature range covered by the data. This maximum can be located pretty definitely at about 135° K. for aluminium. In the case of the other three metals, it becomes progressively more difficult to fix upon a definite temperature as the location of the maximum, the graph being practically a horizontal straight line over an increasingly larger range of temperatures. In other words, the effective average frequency of the oscillators has a practically constant value over a wide range of temperatures. This frequency (in wave-numbers) is 206 for aluminium, 167 for copper, 113 for silver and 50 for lead.

The shape of the graph at low temperatures recalls the course of the graph in the case of diamond already described and discussed in detail in the earlier paper already cited. It is sufficient here to remark that the progressively steeper fall of the graph to low frequencies with the fall of temperature is a consequence of the contribution to the specific heat made by the atomic vibrations of higher frequencies dropping out progressively, until finally at the lowest temperatures we are left only with the contribution made by the vibrations of the very lowest frequencies.

The horizontal stretch of the curves in the middle parts of the temperature range is very clearly analogous to that appearing in the case of diamond throughout the higher parts of the temperature range. Hence, as in the case of diamond, we infer that in this region the effective average frequency of the atomic oscillators is the same or nearly the same as the arithmetical average of the atomic vibration frequencies, the latter term having the same significance as in the discussion of the data for diamond.

5. Frequency Changes at the Higher Temperatures

We turn next to consider the course of the curve in the higher parts of the temperature range. We may reject any interpretation of the features which it exhibits as arising from errors in experimental data. For, the same phenomenon is shown by all the four metals in the same temperature range but to different extents, as is to be expected. Hence, the only possible interpretation of the drop in the effective average frequency at the higher temperatures shown by the graphs is that the atomic vibration frequencies are themselves a function of the temperature and progressively diminish as the temperature rises. It is not possible from the specific heat data to infer what the rate of such diminution is in the lower parts of the temperature range. But we can definitely infer from the form of the curves at the higher temperatures that the fall of the atomic vibration frequencies with rising temperature is at first rather slow, but that it accelerates and finally reaches a fairly steady rate at the higher temperatures.

The detailed discussion of the effects thus brought to light by our present analysis is more appropriately dealt with in Part II of the present paper which concerns itself with the theoretical evaluation of the specific heats of metals as a function of temperature. We may, however, briefly record here some numerical results regarding the rate of fall of the atomic vibration frequencies (expressed as a fraction thereof per degree centigrade) which may be deduced from the slope of the graphs in the case of these four metals. As already remarked, this temperature coefficient is not a constant and we have therefore to consider its value in the vicinity of some temperature at which

the graph has a fairly uniform slope. The values deduced in this way are given below in round figures, and represent the quantity $\frac{1}{\nu}\frac{\Delta\nu}{\Delta T}$, ν being hte effective average frequency of the atomic oscillators. The figures for copper, silver and lead indicate a rather steep increase in the temperature coefficients of the atomic vibration frequencies with increasing atomic mass.

Substance	Atomic Weight	Temperature	Temperature Coefficient of Frequency
Aluminium ..	27·0	255° K.	10×10^{-4} per degree
Copper	63·6	250° K.	6×10^{-4} ,, ,,
Silver	107·9	270° K.	21×10^{-4} ,, ,,
Lead .. .	207·2	215° K.	99×10^{-4} ,, ,,

6. SUMMARY

The specific heat data in the temperature range from 15° to 300° reported by Giaque and collaborators for the four metals aluminium, copper, silver and lead are analysed and the effective average frequency of the atomic oscillators deduced therefrom is plotted as a function of the temperature. The graphs exhibit a steep fall of the effective frequency at very low temperatures as is to be expected. In the middle part of the temperature range, the frequency exhibits a broad maximum which in spectral wave-numbers is respectively 206, 167, 113 and 50 for the four metals. At higher temperatures the graph exhibits a second fall which indicates that there is a real and progressive diminution of the actual vibration frequencies of the atoms in the crystal with rising temperature in this range. The effect becomes increasingly more pronounced with increasing atomic mass.

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THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS

Part II. Approximate Theoretical Evaluation

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(*Memoir No.* 93 *from the Raman Research Institute, Bangalore-6*)

Received January 3, 1957

1. Introduction

In this second paper of the series, we consider the problem of evaluating the specific heats of the four metals aluminium, copper, silver and lead, making use of the theroretical ideas set forth in an earlier paper in these *Proceedings*.[1] The metallic atoms in all these four cases are located at the equivalent points of a simple Bravais lattice of which the unit cell is a rhombohedron. Accordingly, all the normal modes of vibration are of the second kind, namely, those in which the successive atoms along one, two or all the three axes of the lattice oscillate with equal amplitudes but with opposite phases. By simple inspection of a model of the structure, it can be seen that the twenty-one possible normal modes of this kind group themselves into only four distinct modes with 3, 6, 4 and 8 as their respective degeneracies. These may be described in simple geometric terms: oscillations of the atoms in the cubic planes along the normals to those planes (degeneracy 3); oscillations of the atoms in the cubic planes tangential to those planes (degeneracy 6); oscillations of the atoms in the octahedral planes normal to those planes (degeneracy 4); oscillations of the atoms in the octahedral planes tangential to those planes (degeneracy 8). Accordingly, the specific heat of these metals is obtained by a summation of the Einstein functions for the frequencies of these four modes multiplied by their respective degeneracies. To this must be added the contribution arising from the spectrum of vibrational frequencies with a statistical weight of three arising from the three translations of the unit cell with the 8 atoms at its corners. This contribution appears as an integration of Einstein functions taken over a continuous spectrum of frequencies, the upper limit of frequency in the integration being the lowest of the four characteristic frequencies.

2. Evaluation of the Characteristic Frequencies

Each of the atoms in a face-centred cubic lattice has twelve nearest neighbours, six second neighbours, twenty-four third neighbours and twelve

fourth neighbours. The six constants needed to determine the force on any one atom resulting from the displacement of another atom reduce, by virtue of the symmetry of the structure, to *three* constants in the case of the nearest neighbours, *two* constants for the second neighbours, *four* constants for the third neighbours and so on. Thus, even if only the first three sets of neighbours are considered, the equations of motion of an atom would involve nine force-constants arising from the displacements of the surrounding atoms. In the absence of any knowledge regarding the magnitudes of these nine constants, it is not possible to evaluate the four frequencies which we need to know. In the case of diamond dealt with in an earlier paper in the *Proceedings*, it was possible to proceed on the basis of its known spectroscopic behaviour and to make an independent evaluation of the eight characteristic frequencies of vibration of its structure. It is obvious that a different procedure has to be adopted in the case of the metallic elements.

What we have to ascertain are the frequencies of vibration of the atomic *layers* lying respectively in the cubic and octahedral planes normally or tangentially to themselves. It is evident that the frequencies of such vibration would depend on the integrated effect on any one *layer* of the movements of the neighbouring layers. Various considerations indicate that the force acting on any layer would be determined *principally by the displacements relatively to that layer of the two neighbouring layers lying one on either side of it.* By way of justifying this statement, we remark that the first, second and third neighbours of any one atom are mostly to be found either in the same layer or in the two adjacent layers. For instance, in the cubic layers all the twelve near neighbours, four out of the six second neighbours and sixteen out of the twenty-four third neighbours are to be found thus located. Likewise, in the octahedral layers all the twelve near neighbours, all the six second nearest neighbours and eighteen out of the twenty-four third neighbours are to be found thus located. Hence, the frequencies of oscillation with which we are concerned may *as a first approximation* be evaluated on the basis that the forces on any one layer arise only from the displacements relative to it of the two neighbouring layers, one on either side of it.

For the same reasons as those explained above, the forces which determine the velocities of elastic wave propagation in the cubic and octahedral directions would likewise be determined *as a first approximation* by the displacements relative to any layer of the two neighbouring layers one on either side. Hence, we are in a position to establish simple but approximate relationships between the characteristic frequencies of vibration of the

lattice and the velocities of propagation of elastic waves (longitudinal or transverse as the case may be) in the directions normal to the cubic and octahedral planes respectively. This relation may be written as below:

$$\text{Characteristic frequency} = \frac{2}{\pi} \cdot \frac{\text{Velocity of long elastic waves}}{\text{Twice the distance between adjacent layers}}.$$

The correctness of the formula is easily verified by comparison with the case of a simple linear lattice, *viz.*, a string under tension loaded with identical mass-particles at equidistant intervals.

3. Numerical Results

The foregoing approximate relationships between the velocity of propagation of elastic waves along the octahedral and cubic axes and the characteristic frequencies of a face-centred cubic lattice enable us to evaluate the latter for those crystals for which the elastic constants have been determined with precision. The published determinations make use of the three constants C_{11}, C_{12} and C_{44} contemplated in Voigt's theory. The four velocities we are concerned with are the square roots of C_{11}/ρ, C_{44}/ρ

$$(C_{11} + 2\,C_{12} + 4\,C_{44})/3\rho \quad \text{and} \quad (C_{11} - C_{12} + C_{44})/3\rho.$$

In the cases of aluminium[2] and copper,[3] the values of C_{11}, C_{12} and C_{44} are available over a wide range of temperatures from the very lowest upwards. They exhibit a progressive diminution with temperature, which at first is slow but accelerates at high temperatures. In the cases of silver[4] and lead,[5] however, determinations of the elastic constants only at room temperatures are available and we shall make use of them.

TABLE I

Characteristic frequencies in wave-numbers

Mode	Degeneracy	Aluminium		Copper		Silver	Lead
I	3	353	340	260	255	179	88
II	6	177	169	177	171	109	48
III	4	287	302	269	263	179	87
IV	8	145	138	113	109	70	30
Average	..	211	207	182	177	117	54

Table I shows the four characteristic frequencies calculated in the manner explained above. In the cases of aluminium and copper, the values are given at absolute zero as also at room temperature, while in the case of silver and lead, only room temperature values are given. Multiplying the frequencies by the degeneracies of the respective modes, then adding up and dividing by 21, we get the arithmetical average of the four frequencies. This is shown at the foot of the table in each case.

As the elastic constants diminish with increasing temperature but not all in the same manner, it is not altogether surprising to find that one of the calculated frequencies for aluminium actually increases instead of diminishing with rise of temperature. However, both for aluminium and for copper the arithmetical average shows a noticeable fall at room temperature as compared with the value at the absolute zero.

4. CALCULATION OF THE SPECIFIC HEATS

The expression for the thermal energy of the crystal is given by the formula

$$\frac{N}{8}\left\{\sum_{i=1}^{i=4}\frac{h\nu_i}{e^{h\nu_i/kT}-1}+\frac{3}{\nu_4^3}\int_0^{\nu_4}\frac{h\nu}{e^{h\nu/kT}-1}3\nu^2\,d\nu\right\}$$

where N is the number of lattice cells contained in the volume of the crystal under consideration. Differentiating this with respect to T, we obtain the specific heat of the crystal at any given temperature. In evaluating the same, we make use of the tabulated values of the well-known functions appearing in the expressions.

The values of the specific heat have been plotted as functions of the absolute temperature in the lower of the two graphs in Figs. 1, 2, 3 and 4 which refer respectively to the four metals. As usual, the abscissæ are the absolute temperatures, and the scale of ordinates for the specific heat appears on the left-hand side of the figure in each case. The upper graph in each figure is the effective average frequency determined from the calculated specific heat in the manner already explained in the previous papers. The scale of ordinates for this frequency appears on the right-hand side of the figure in each case and is expressed in wave-numbers.

It will be noticed that at the upper end of the temperature range in each of the four cases, the effective average frequency of the atomic oscillators deduced from the calculated specific heats is respectively 210, 182, 117 and 55 cm.$^{-1}$ It will also be noticed that these are equal respectively to the

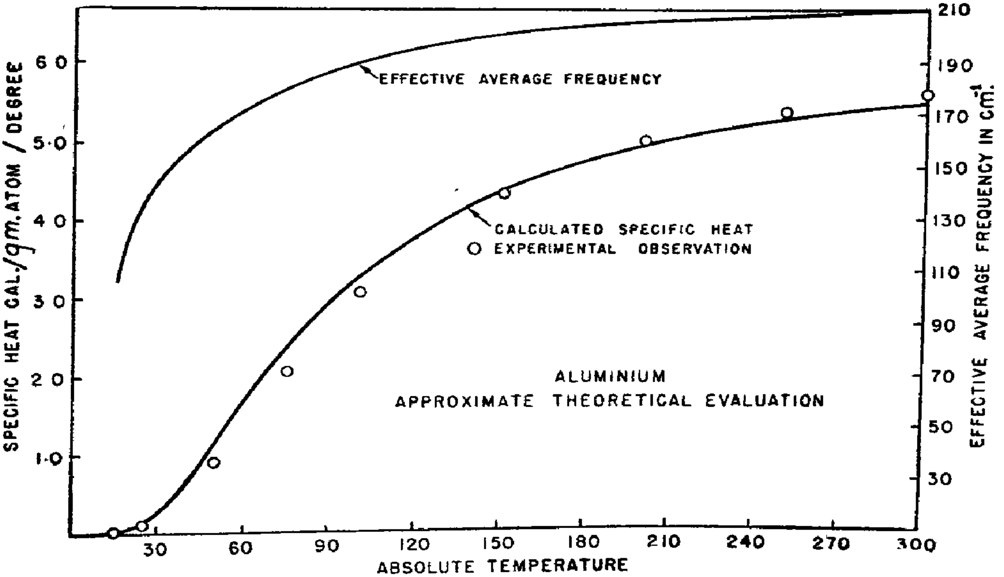

FIG. 1. Specific Heats of Aluminium.

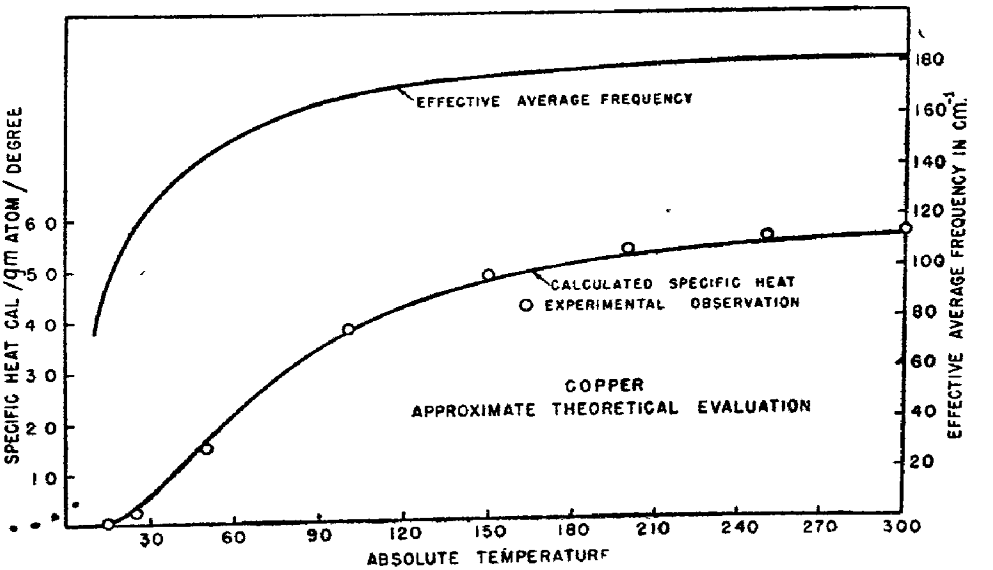

FIG. 2. Specific Heats of Copper.

arithmetical average of the four characteristic frequencies of each metal shown at the foot of Table I. The effective average frequency falls off quite slowly as the temperature goes down and hence in the upper part of the temperature range, the arithmetical average frequency determines the course of the specific heat curve. Hence any assumption, however arbitrary, regarding the nature of the atomic vibration spectrum would give the specific heat correctly in this part of the range, provided it gives the same arithmetical average for the atomic vibration frequencies. It is only the steeply falling part of the specific heat curve that is sensitive to the precise nature of the assumed vibration spectrum and can furnish reliable information regarding its true complexion.

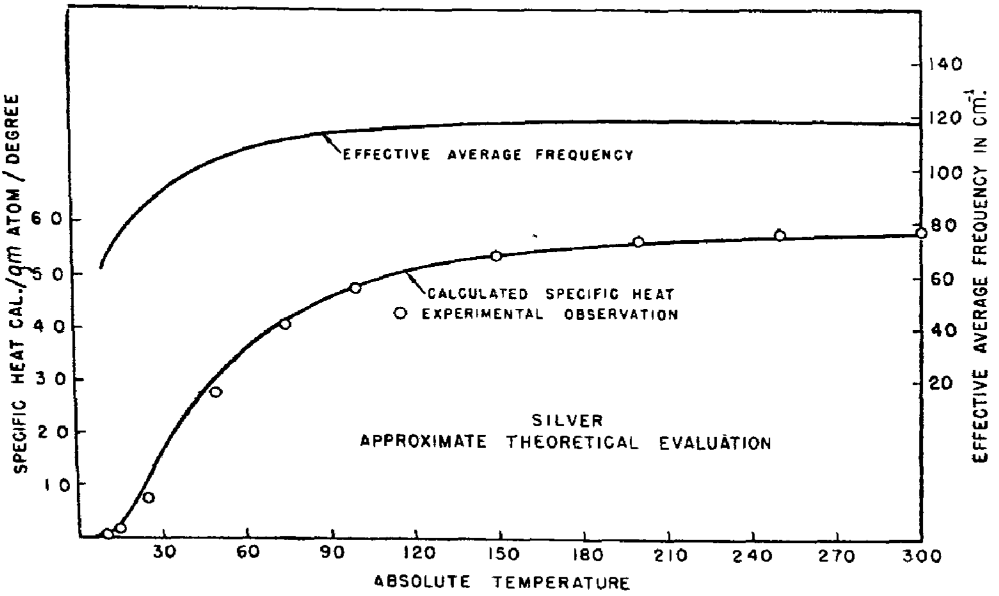

FIG. 3. Specific Heats of Silver.

5. DISCUSSION OF THE RESULTS

In Part I of the present series of papers,[6] an analysis of the results of the specific heat determinations by Giaque and his collaborators for these four metals was presented and graphs were reproduced showing the effective average frequency as a function of the temperature. These graphs, unlike those appearing in the present paper, do *not* appear as nearly horizontal lines in the upper part of the temperature range in each case, but exhibit a

plateau* in the middle part of the range and then slope down to lower values at the upper limit of the range. It is to be inferred from these consequences deduced from the actual specific heat determinations that the atomic vibration frequencies are themselves not independent of the temperature, and that they (or at least their arithmetical averages) diminish progressively as the temperature rises.

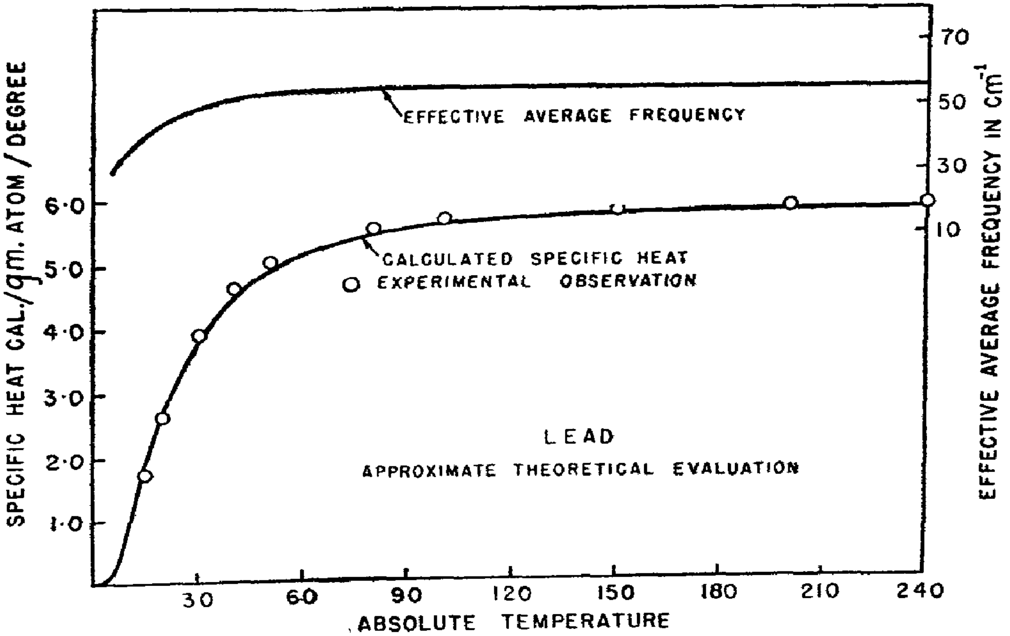

FIG. 4. Specific Heats of Lead.

The experimentally determined specific heats[7,8] have been plotted alongside of the graphs of the calculated specific heats in Figs. 1, 2, 3 and 4 of the present paper. In view of the remarks made above, it is to be expected that the observed specific heats would lie above the calculated ones in the upper part of the temperature range. It will be noticed from the figures that this is actually the case. The deviations are fairly conspicuous in the case of aluminium and copper, but are less conspicuous in the cases of silver and lead. The characteristic frequencies for aluminium and copper were calculated from the low-temperature elastic constants, while for silver and lead the frequencies were calculated from the elastic constants at room

* The plateau frequencies are 206, 167, 113 and 50 cm.$^{-1}$ respectively for aluminium, copper, silver and lead. These are somewhat smaller than the arithmetical average frequencies, as is to be expected.

temperature. The closer approximation actually found between the observed and the calculated specific heats for silver and lead at the higher temperatures is therefore to be expected.

Having regard to the method used for evaluating the four characteristic frequencies, and remembering also that in the present theory we have totally disregarded the anharmonicity of the atomic oscillators, the general agreement between theory and observation over the entire range of temperatures exhibited by Figs. 1 to 4 may be considered satisfactory. However, it is to be remarked that the observed specific heats are sensibly lower than the calculated ones in the range of temperatures where the specific heat curve slopes steeply down. This is noticeable in the cases of all the four metals and indicates that the characteristic frequencies as determined by the present approximate method need revision. We shall return to this in the third paper of the series.

6. SUMMARY

The specific heats of the four metals aluminium, copper, silver and lead which crystallise as face-centred cubic lattices are evaluated in terms of the four characteristic frequencies of vibration of such a lattice, these latter being determined by an approximate method which relates them to the elastic constants of the crystal. The results thus derived are discussed and compared with the experimentally determined specific heats.

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THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS

Part III. The Characteristic Frequencies

BY SIR C. V. RAMAN

(Memoir No. 93 from the Raman Research Institute, Bangalore-6)

Received February 9, 1957

1. INTRODUCTION

IN Part I of the present series of papers, the experimental data for the specific heat at constant volume of the four metals aluminium, copper, silver and lead were analysed and discussed. The method of analysis was a determination, with the aid of a table of Einstein's specific heat function, of the frequency of atomic vibration which, if assumed to be common to all the atomic oscillators, would give for the specific heat of the solid its observed value at any given temperature. The frequency thus determined is termed the effective average frequency of the atomic oscillators and is itself a function of the temperature. When this is represented as a graph, it discloses a progressive diminution of the frequency in the upper part of the temperature range covered by the data. Considered in relation to the atomic vibration frequencies themselves, this diminution is least conspicuous in the case of *copper*, while the three other metals aluminium, silver and lead form a sequence in which it exhibits an increasing magnitude.

The explanation of these results is not far to seek. The Einstein formula for the energy of an atomic oscillator as a function of its frequency and the expression for the specific heat deduced therefrom by differentiation rest on the assumption that the oscillators are *harmonic*. This assumption is however not strictly justifiable. The expansion of volume which all the metals exhibit with rise of temperature can only be understood if we recognize that the atomic oscillators which are the carriers of the thermal energy are anharmonic in their modes of vibration. Such anharmonicity implies that the vibration frequencies of a quantised oscillator do not form a harmonic sequence but that the successive increments of frequency fall off in a regular progression. Simultaneously also, the dimensions of the oscillator would exhibit a progressive increase which is connected with the magnitude of the vibration and its anharmonicity and hence also with the changes of frequency in a quantitative fashion. It is worthy of remark in this connection that the volume expansion between 0° and 300° absolute

in the case of the four metals under consideration is least for *copper*, being 1%, while the three other metals, aluminium, silver and lead form a sequence in which it progressively increases, being 1·2%, 1·3% and 2·2% respectively for these metals. Thus, there is a clear correlation between the rate of thermal expansion and the rate of change of the atomic vibration frequencies which these metals exhibit at higher temperatures as deduced from their specific heat data.

As is well known, the thermal expansion coefficient of a metal tends to zero at the lowest temperatures and at higher temperatures increases *pari passu* with the specific heat. It follows from these facts and the remarks made above that the specific heats of these metals can be adequately represented by a summation of the Einstein functions for frequencies assumed to be independent of the temperature only over the limited part of the temperature range where the overall expansion of the solid is small and may be ignored without sensible error.

In Part II of the present series of papers, the characteristic frequencies for the four metals were evaluated *by an approximate method* based on their relationship to their elastic constants. As was remarked in that paper, the specific heats thus calculated showed distinct deviations from the observed values in the steeply falling part of the curve where its course is specially sensitive to the values chosen for the frequencies. The need for a more precise evaluation was thereby rendered evident. In the present paper, it will be shown that this revision may be effected by making use of the specific heat data themselves in the lower part of the temperature range.

2. THE CHARACTERISTIC FREQUENCIES

Table I below gives the four characteristic frequencies for the four metals calculated approximately from their elastic constants and used in Part II. In the adjacent columns are shown the revised values adopted in the present paper. The latter have been determined by trial so as to give the best possible fit with the actual course of the specific heat curve in the lower part of the temperature range in each case. Multiplying each frequency by its degeneracy and dividing the sum total by 21, we obtain the average frequency of the atomic oscillators and this is also shown at the foot of each column.

On an examination of the figures in Table I, it will be seen that in all the four cases, the frequencies as now revised exhibit certain general features in common. Their magnitudes follow each other in the order I, III, II and IV. This is also the order to be expected theoretically, for the

TABLE I

Characteristic frequencies in $cm.^{-1}$

Mode	Degeneracy	Aluminium		Copper		Silver		Lead	
		From elastic constants	From specific heats	From elastic constants	From specific heats	From elastic constants	From specific heats	From elastic constants	From specific heats
I	3	353	340	260	250	179	179	88	80
	6	177	200	177	185	109	125	48	45
III	4	287	290	269	215	179	155	87	80
IV	8	145	160	113	120	70	80	30	34
Average ..		211	222	182	175	117	121	54	53

cubic spacings are smaller than the octahedral ones and hence should correspond to higher frequencies of vibration, while the longitudinal oscillations in each case should have a notably higher frequency than the transverse ones. Comparing the frequencies determined from the specific heat data with the approximate values estimated from the elastic constants, we also notice certain general features: the frequency of mode I as now deduced is slightly smaller in all the cases; the frequency of mode II is slightly larger in all the cases except lead; the frequency of mode IV is distinctly larger in all the four cases, while the frequency of mode III is notably diminished in all the cases except aluminium. These alterations have resulted in an increase by a few per cent. of the average of the frequencies for aluminium and silver and a diminution by a few per cent. of the average in the cases of copper and lead. They have also resulted in bringing the four frequencies for each metal into the proper relationships with each other to be expected in physical grounds, already remarked.

3. THE EVALUATION OF THE SPECIFIC HEATS

Using the values of the characteristic frequencies now adopted, the specific heat for each of the four metals has been calculated by summing up the Einstein functions for the four frequencies and adding the contribution from the continuous spectrum, the upper limit of frequency for the latter being the same as the lowest of the four characteristic frequencies. From the specific heats thus evaluated, the effective average frequencies of the atomic oscillators has also been evaluated as a function of temperature,

In Figs. 1, 2, 3 and 4 above, these calculations have been represented graphically. The abscissæ in the graphs are the absolute temperatures, while the ordinates for the specific heats and for the effective average

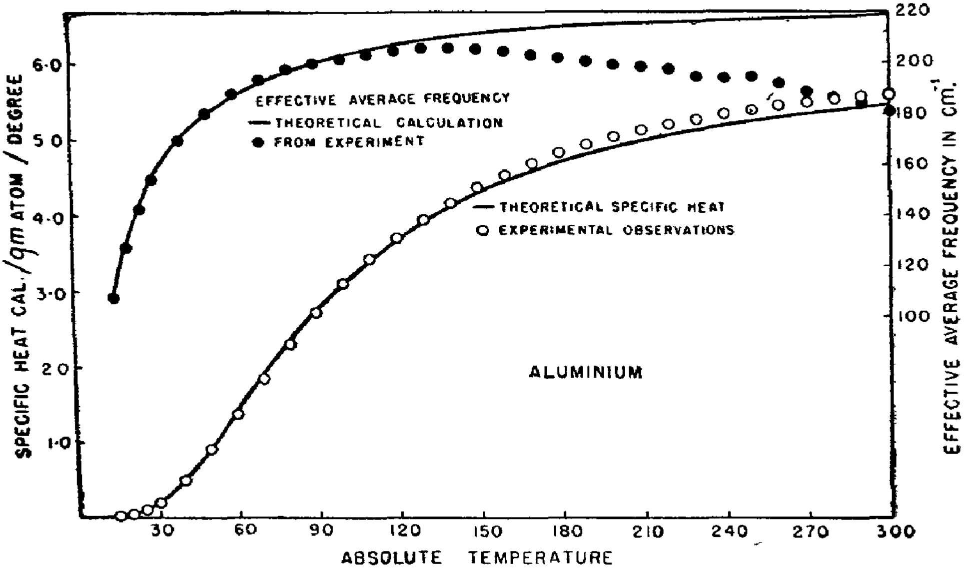

FIG. 1. Specific Heats of Aluminium.

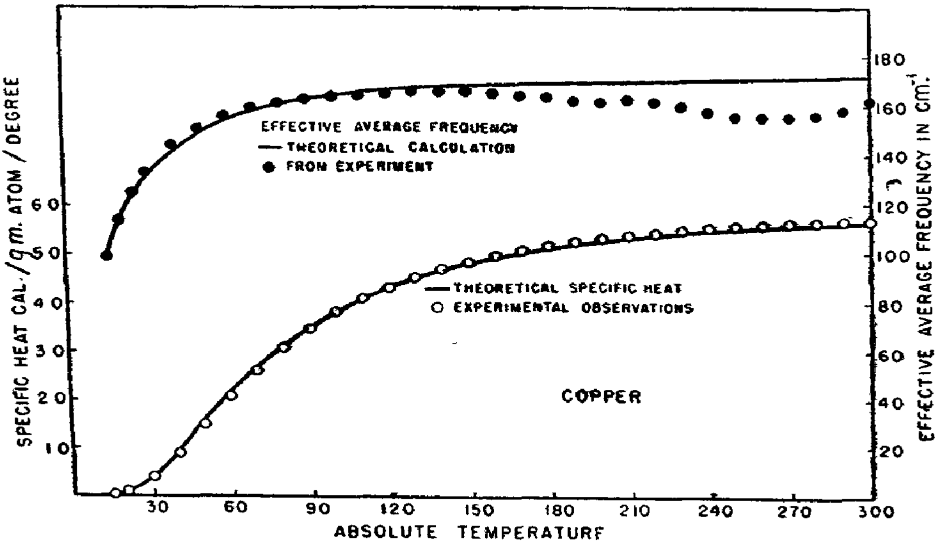

FIG. 2. Specific Heats of Copper.

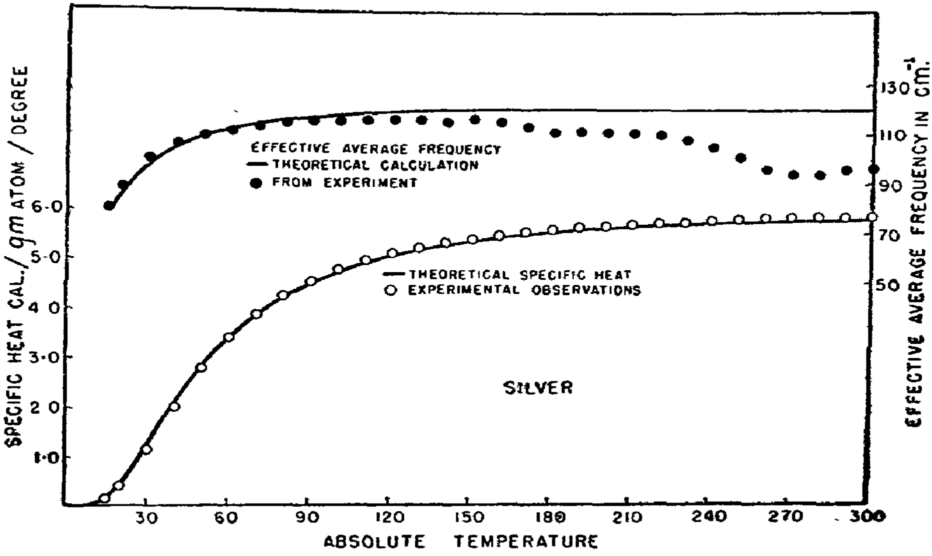

FIG. 3. Specific Heats of Silver.

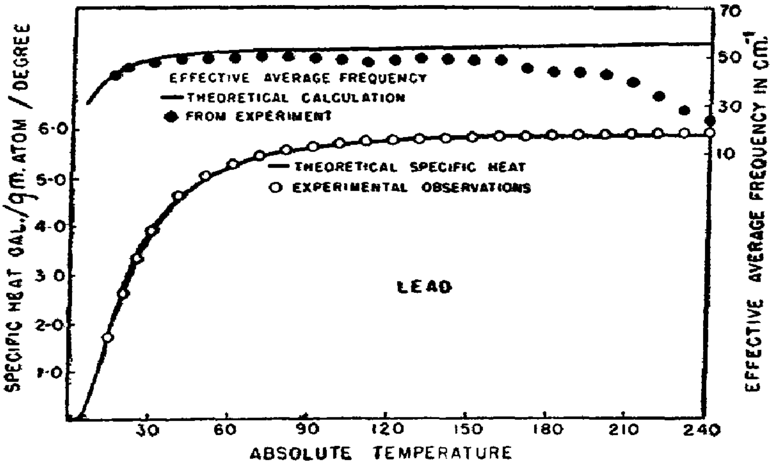

FIG. 4. Specific Heats of Lead.

frequencies appear respectively on the left- and right-hand sides of the figure. It will be seen that the effective average frequency at the upper end of the temperature range is practically the same as the arithmetical average frequency shown at the foot of the columns in Table I in each case.

The experimentally determined values of the specific heat and the effective average frequencies calculated therefrom have also been shown in the graphs alongside of the theoretically computed curves in Figs. 1, 2, 3 and 4. As already stated, the characteristic frequencies employed for the calculation were so chosen as to give the best possible fit with the specific heats in the lower part of the temperature range, *i.e.*, between 15° and 150° absolute in each case. It will be seen that in this part of the temperature range, the observed values fall close to the theoretical curves. On the other hand, in the upper part of the temperature range, *i.e.*, between 150° and 300° absolute, the specific heats observed are consistently higher than the calculated values. The reason for this is evident from the plots of the effective average frequency of atomic vibration. In all the four cases, the atomic vibration frequencies actually effective in the upper part of the temperature range are no longer those deduced from the specific heats at low temperatures but show a progressive diminution with rise of temperature, for the reasons already explained in the Introduction.

SUMMARY

The specific heat data themselves enable us to evaluate more precisely the four characteristic frequencies of each metal determined approximately in Part II from their elastic constants. Making use of the new values, the complete specific heat curve is theoretically deduced and shows good agreement with the observations in the lower part of the temperature range, but deviates observably in its upper part, as is to be expected in view of the progressive fall in the frequency of the atomic oscillators with rise of temperature indicated by the analysis of the data in Part I. This diminution of the frequencies is a consequence of the anharmonicity of the oscillators which also results in the thermal expansion of the metal. Copper, aluminium, silver and lead form a sequence in the order of increasing coefficients of thermal expansion as also in the magnitude of the temperature coefficients of atomic vibration frequency indicated by their specific heat data.

THE SPECIFIC HEATS OF SOME METALLIC ELEMENTS

Part IV. The Residual Spectrum

By Sir C. V. Raman

(*Memoir No.* 93 *from the Raman Research Institute, Bangalore* 6)

Received February 25, 1957

1. Introduction

The theory of the specific heats of crystals developed in a recent paper by the present author is based on the result that the structure of a crystal containing p atoms in each unit cell has $(24p - 3)$ normal modes of vibration characterised by sharply defined monochromatic frequencies. These may be described as the modes of internal vibration of the groups of $8p$ atoms each included in volume elements of the crystal whose dimensions are twice as large in each direction as those of the unit cell. The three degrees of freedom of atomic movement left out in this description represent the three translations of each group of $8p$ atoms. The vibration spectrum resulting from these translations may be designated as " the residual spectrum " and its nature was discussed in the paper already cited. The contribution to the thermal energy of the crystal arising from the translations of each group of $8p$ atoms is represented by an integral in which Einstein's expression for the average energy of an oscillator of frequency ν appears multiplied by a quantity $9 . \nu^2 d\nu / \nu_l^3$ and the product is integrated between the limits 0 and ν_l. The upper limit is the upper limit of frequency in the residual spectrum and is also the lowest of the $(24p - 3)$ frequencies characteristic of the structure.

In the case of the metallic elements now under consideration, $p = 1$ and the residual spectrum thus represents only 3 out of every 24 degrees of atomic freedom of movement. It nevertheless plays a major role in determining the magnitude of the specific heat of the metals at very low temperatures. Hence, a comparison of the experimental data at such low temperatures with the calculated values is of importance for establishing the correctness of the present approach to the theory of their specific heats. It is the object of the present paper to present the results of such a comparison.

As the determinations by Giaque and his collaborators which have so far been the basis of our discussion stop at 15° K., we have necessarily to make use of the results reported by other investigators for still lower temperatures. The circumstance that the specific heats at such temperatures are very low and increase rapidly with rise of temperature sets a limit to the

possible accuracy of their experimental determinations. The specific heat also varies enormously from metal to metal and hence even a small percentage of impurity would affect the determined values, raising them or lowering them, as the case may be. These factors may be responsible for the divergences noticed between the results reported by Giaque and collaborators and those obtained by other investigators in the temperature ranges common to them. These divergences are particularly large in the case of aluminium which has a very low specific heat in the range 0 to 15° K. but are less serious in the case of the other three metals, copper, silver and lead.

2. THE ELECTRONIC SPECIFIC HEATS

The observed variation of the specific heats of metals with temperature in the vicinity of the absolute zero differs in its features from that observed in the case of insulators, *e.g.*, diamond or the alkali halides. The curves do not touch the axis of the abscissæ but meet it at the origin making a definite angle with it. The specific heats in this region can be represented by an expression of the form $AT + BT^3$. These facts are explained on the basis that the first term represents the contribution arising from the thermal agitation of the electrons and the second from the thermal agitation of the atoms themselves. This interpretation finds support in the fact that in the case of metals exhibiting superconductivity, *e.g.*, aluminium and lead, the coefficient A exhibits a distinctly larger value in the range of superconductivity, while the coefficient B remains unaltered.

TABLE I

Specific Heats at Low Temperatures

$c_v = AT + BT^3$

Substance	Range of measurement	$A \times 10^4$	$B \times 10^5$	Author
Aluminium ..	0–20° K. 0– 4° K.	3·48 3·42	0·63 0·68	Kok & Keesom Howling *et al.*
Copper ..	0–20° K. 0– 5° K.	1·78 1·64	1·24 1·14	Kok & Keesom Corak *et al.*
Silver ..	0– 5° K.	1·46	4·06	Corak *et al.*
Lead ..	0– 5° K.	7·48	52·04	Horowitz *et al.*

Table I shows the results for the four metals now under consideration reported by various authors. It will be seen that the coefficient A is largest for lead; aluminium stands next and is followed by copper and silver, the coefficients for the latter not being very different. The value quoted in the case of lead is for the state of the metal in which the superconductivity has been eliminated by a strong magnetic field.

It follows from what has been stated above that for a comparison of the experimental data with the results of the present theory, it is necessary to add to the specific heat a term representing the electronic contribution. This has been done, making use of the results of the authors quoted in the table. We shall discuss first the results thus obtained in the case of copper, silver and lead, since in the cases of these metals the determinations which we make use of are in reasonable agreement with those reported by Giaque and collaborators. The case of aluminium where this is not the case will also be discussed.

3. Comparison of Theory and Experiment

Copper.—The specific heat of copper in the range between 0° and 20° K. has been reported by Kok and Keesom, while in the more limited range

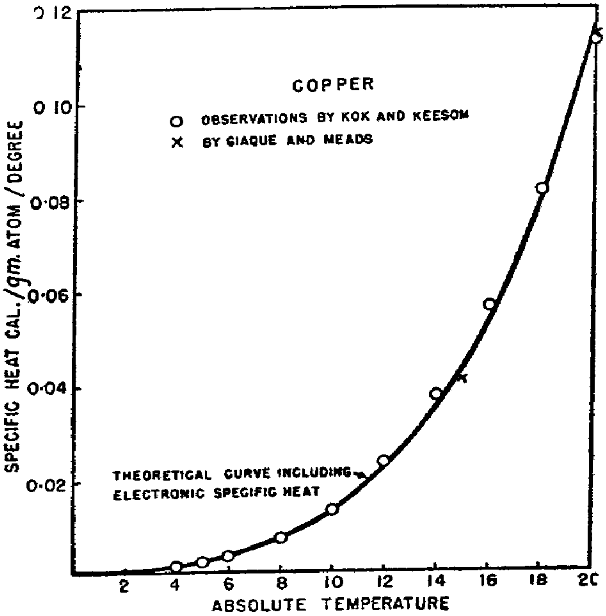

Fig. 1. **Specific Heats of Copper.**

from 0 to 5° K., measurements have been made by Corak, Garfunkel, Satterthwaite and Wexler. We present the comparison between theory and experiment in the form of two graphs, one in the range 0 to 20° K. and the other in the range 0 to 5° K. In the latter range the results of Kok and Keesom are systematically in excess of those reported by Corak *et al.*, the difference being about 8% at 5° K. However, a satisfactory overall agreement between theory and experiment is exhibited by both the graphs.

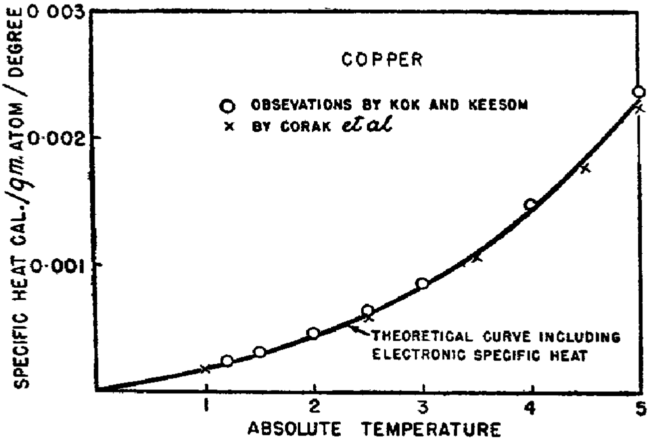

FIG. 2. Specific Heats of Copper.

Silver.—Likewise in the case of silver we present the results in the form of two graphs, Figs. 3 and 4 respectively. Here again, a satisfactory agreement emerges between the theoretical results and the experimental data.

Lead.—All the four characteristic frequencies besides the residual spectrum contribute to the observed specific heat at 20° K. and this continues to be the case upto 10° K. At still lower temperatures the contributions of only the lowest of the four characteristic frequencies and the residual spectrum predominate. Below 5° K., only the residual spectrum is of importance. As in the previous cases we present a comparison between theory and experiment in the form of two graphs covering the ranges 0 to 20° K. and 0 to 5° K. as Figs. 5 and 6 respectively. In Fig. 5 the available determinations of various authors have all been plotted and it will be seen that between 15° and 20° K. the determinations agree generally with each other and with the course of the theoretical curve. Between 5° and 15° K. the only observations are those by Keesom and Van den Ende whose results appear to be rather erratic but nevertheless follow the trend of the theoretical curve fairly well. At the lowest temperatures the results of these same authors are notice-

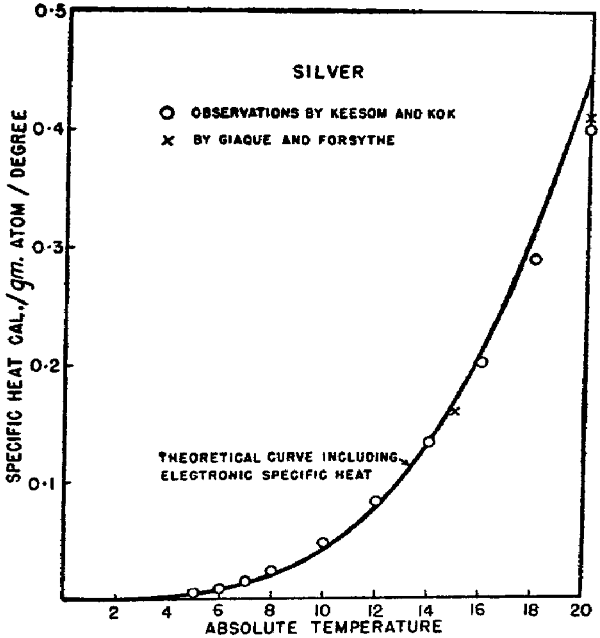

Fig. 3. Specific Heats of Silver.

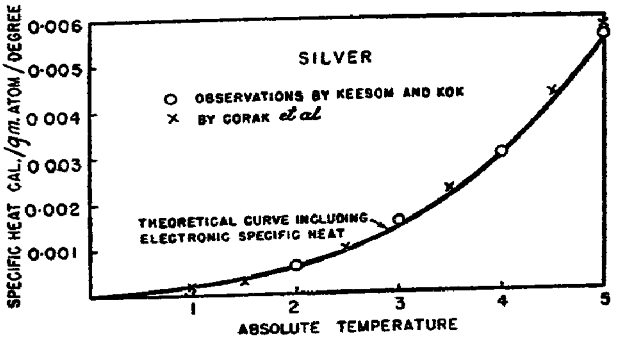

Fig. 4. Specific Heats of Silver.

ably in excess of those deduced from theory. But as will be seen from Fig. 6 the observations by Horowitz *et al.* are in excellent accord with the calculated values.

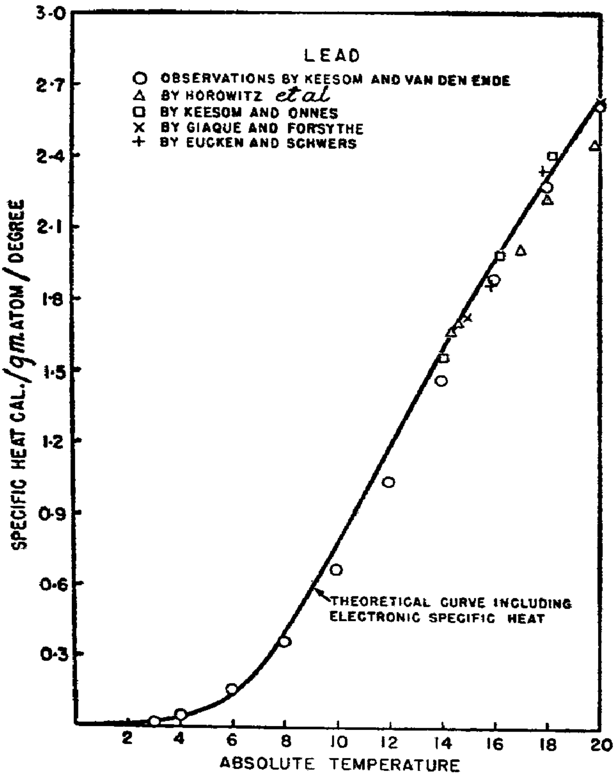

FIG. 5. Specific Heats of Lead.

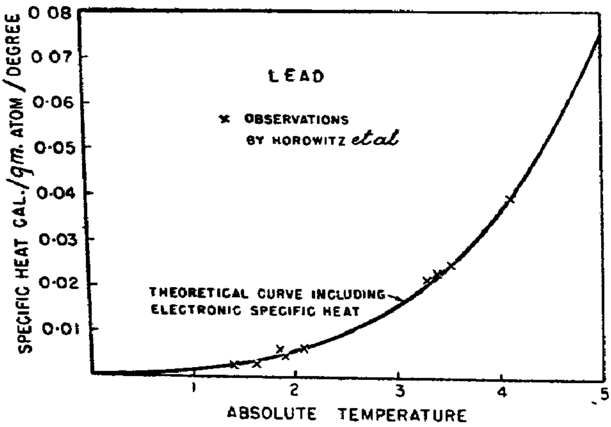

FIG. 6. Specific Heats of Lead.

Aluminium.—Of the four metals studied, aluminium has the lowest specific heats in the range 0 to 20° K., and the electronic contribution forms an important part of the whole. Making use of the characteristic frequencies deduced in Part III from the specific heat data themselves as reported by Giaque and Meads and taking into account the electronic contribution, the specific heat curve has been computed. The graph thus obtained coincides with the observations reported by Kok and Keesom only at the lowest temperatures where the electronic heat contribution predominates. In the range from 5 to 20° K., the data reported by Kok and Keesom deviate progressively from the theoretical curve, the observed values being everywhere in excess by quantities ranging from 8 to 20% of the calculated ones. They are also in excess of the values reported by Giaque and Meads for 15° and 20° K. to a similar extent.

Throughout the range now under discussion the specific heat of aluminium is determined solely by the contribution of the residual spectrum with the addition of the electronic specific heat. The values reported by Kok and Keesom throughout the range would be in fair agreement with the theoretical calculations if the upper limit of frequency in the residual spectrum were taken as 146 cm.$^{-1}$ which is nearly the value deduced in Part II by an approximate method instead of as 160 cm.$^{-1}$ calculated in Part III from the specific heat data themselves. But the former assumption would result in the theoretically calculated values at higher temperatures differing from those reported by Giaque and Meads by more than the probable magnitude of their experimental errors. Considering these facts, it appears correct to assume that the values reported by Kok and Keesom for aluminium in the upper part of the temperature range between 0 to 20° K. are in excess of the real values by quantities of the order of 10%.

Summary

The theoretical calculation of the specific heats of the four metals aluminium, copper, silver and lead which in Part III were shown to be in satisfactory accord with the experimental data reported by Giaque and collaborators in the range from 15 to 300° K. have in the present paper been extended down to the absolute zero. When the contribution arising from the thermal agitation from the electrons is included, the calculated specific heats are in satisfactory accord with the results reported by various investigators on the low temperature specific heats of these metals. The agreement is excellent in the cases of copper, silver and lead, but not so satisfactory for aluminium, the available data for which are meagre and appear to be of doubtful accuracy.

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Reprinted from "The Proceedings of the Indian Academy of Sciences",
Vol. XLV, No. 3, Sec. A, 1957

THE OPTICAL ROTATORY DISPERSION OF QUARTZ

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(*Memoir No. 94 from the Raman Research Institute, Bangalore-6*)

Received January 2, 1957
(Communicated by Sir C. V. Raman)

ABSTRACT

Many formulæ have been proposed to express numerically the rapid increase of the rotatory power of quartz with decrease of wavelength. An examination of these formulæ shows that they are wholly inappropriate for the case of quartz. It has been shown that the entire range of data from the visible to the extreme ultraviolet is accurately represented by a new type of formula involving only two constants, *viz.*,

$$\rho = \frac{k\lambda^2}{(\lambda^2 - \lambda_0{}^2)^2},$$

where $k = 7 \cdot 19$ and $\lambda_0 = 0 \cdot 0926283\,\mu$. A theoretical interpretation of the new formula has been given on the basis of a simple coupled oscillator model.

INTRODUCTION

THE phenomenon of optical activity was discovered in the year 1811 by Arago in pieces of quartz cut perpendicular to the optic axis. Soon afterwards, Biot showed that the rotatory power in the visible region of the spectrum varies inversely as the square of the wavelength, *i.e.*, $\rho = k/\lambda^2$. The rotatory dispersion of quartz has subsequently been the subject of extensive experimental study. This has been reviewed by Sosman in his book on the properties of silica (1927) and by Lowry in his treatise on optical rotatory power (1935). More recently, measurements have been pursued into the remote ultraviolet upto 1500 Å by Servant (1939). It is evident from these determinations that Biot's Law fails completely as we move away from the visible spectrum. Indeed, from 6000 Å to 1500 Å the rotatory power increases by nearly 40 times instead of 16 times as required by the inverse square formula.

There have been several attempts in the past at expressing the rotatory dispersion in terms of assumed characteristic frequencies. In the present

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paper, these formulæ have been examined and it is shown that they are completely unsatisfactory for the case of quartz. A new type of formula has been suggested, a single term of which fits the whole range of data from the visible to the extreme ultraviolet very accurately. On the basis of a simple coupled oscillator model, a theoretical interpretation has been given to this formula. It is proved that the new formula is not open to the same theoretical objection which disqualifies all the earlier formulæ, which are principally of the Drude type.

EARLIER FORMULÆ FOR THE ROTATORY DISPERSION OF QUARTZ

The first attempt at a theoretical formula for the rotatory dispersion of quartz was made by Drude in his *Lehrbuch der Optik* (1900), where he proposed the form

$$\rho = \sum_r \frac{Q_r}{\lambda^2 - \lambda_r^2}, \tag{1}$$

where ρ is the rotatory power in degrees per millimetre, Q_r is a constant corresponding to the characteristic absorption wavelength λ_r in microns, the summation being performed over all the r absorption frequencies. Drude found that the then available data could be fitted by a two term formula, where

$$Q_1 = 12{\cdot}2, \qquad Q_2 = -\,5{\cdot}046,$$
$$\lambda_1^2 = 0{\cdot}010627, \qquad \lambda_2^2 = 0,$$

the negative term being unambiguously indicated to be necessary.

Lowry (1912) found that Drude's formula is not accurate enough to fit his first series of extended measurements and hence altered it to

$$\rho = \frac{11{\cdot}6064}{\lambda^2 - 0{\cdot}010627} - \frac{4{\cdot}3685}{\lambda^2} + \frac{13{\cdot}42}{\lambda^2 - 78{\cdot}22}, \tag{2}$$

the additional third term corresponding to the infrared absorption band. The later and more accurate readings of Lowry and Coode-Adams (1927) required a further modification of (2), and their final formula is

$$\rho = \frac{9{\cdot}5639}{\lambda^2 - 0{\cdot}0127493} - \frac{2{\cdot}3113}{\lambda^2 - 0{\cdot}000974} - 0{\cdot}1905, \tag{3}$$

where, instead of the single absorption band at 1031 Å used in the previous formulæ, two new characteristic wavelengths at 1129 Å and 312 Å have been used, the effect of the infrared being substituted by a constant.

However, all these formulæ fail to represent the measurements of Duclaux and Jeantet (1926) extending up to 1854 Å. These authors have proposed the formula

$$\rho = \frac{7 \cdot 284}{\lambda^2 - 0 \cdot 015114} \tag{4}$$

to approximately fit their data. But, as the discrepancy with this simple formula is quite considerable even in the near ultraviolet, another was worked out by Bradshaw and Livens (1929), *viz.*,

$$\rho = \frac{845 \cdot 694}{(\lambda^2 - 0 \cdot 01274912)} - \frac{0 \cdot 40235}{(\lambda^2 - 0 \cdot 01274912)^2} - \frac{838 \cdot 4320}{(\lambda^2 - 0 \cdot 0120800)} - \frac{0 \cdot 1331233}{(\lambda^2 - 0 \cdot 0120800)^2} + \frac{43 \cdot 05794}{(\lambda^2 - 80 \cdot 00)} + \frac{2119 \cdot 117}{(\lambda^2 - 80 \cdot 00)^2}. \tag{5}$$

It will be noticed that the rotatory power in this formula is expressed as a difference of two very large terms of nearly equal magnitude but of opposite signs involving two absorption wavelengths respectively at 1129 Å and 1099 Å and that the influence of the infrared has been retained. The formula, however, deviates notably from the newer measurements of Servant (*loc. cit.*) in the far ultraviolet region. Servant (1940) has therefore fitted his results with the expression

$$\rho = 10^4 \frac{10^{-6}\lambda^2 + 0 \cdot 515}{(13 \cdot 956 \times 10^{-2}\lambda^4 - 17639 \times 10^{-6}\lambda^2 + 2 \cdot 076)} \tag{6}$$

where λ is the wavelength of light in vacuum expressed in Å. He has assumed the existence of two characteristic wavelengths, one at 1064 Å, and another at 362 Å. The formula fits the entire data from 7000 Å to 1500 Å well. Later, the same author (1941), realising that a multiterm formula involving numerous unknown constants is very artificial and arbitrary, has rejected (6) in favour of the simpler formula

$$\rho = (n_0^2 + 2) \frac{165 \cdot 6}{10^{-6}\lambda^2 - 1 \cdot 325}, \tag{7}$$

where n_0 is the ordinary refractive index of quartz. The characteristic absorption assumed here lies at 1150 Å. The formula is approximately valid from 8000 Å to 2000 Å and fails farther out in the ultraviolet.

Finally, Radhakrishnan (1947) has proposed the formula

$$\rho = \frac{4 \cdot 948}{\lambda^2 - 0 \cdot 014161} + \frac{4 \cdot 617}{\lambda^2 - 0 \cdot 011236} - \frac{2 \cdot 311}{\lambda^2 - 0 \cdot 000974}$$

$$- \frac{0 \cdot 000815}{(\lambda^2 - 0 \cdot 0195)^2} - 0 \cdot 1905. \qquad (8)$$

This one is largely a refinement on the work of Lowry and Coode-Adams. The absorption at 312 Å is still retained, but the single term at 1129 Å has been split into two terms at 1060 Å and 1190 Å. In addition a square term at about 1400 Å, almost at the limit of continuous absorption of light in quartz, has been introduced. The formula gives a tolerable fit.

Thus we see that a variety of formulæ involving numerous hypothetical absorption frequencies have been suggested to express the rotatory dispersion of quartz. Even a cursory examination of these formulæ shows that most of them are extremely complicated and arbitrary in character and all, except one, are unsatisfactory in accounting for the actual observed facts. Apart from this, there is an even more serious objection which may be raised against them.

KUHN'S SUMMATION RULE

A fundamental theorem concerning the optical rotatory power of molecular systems was derived by Kuhn (1929) in the first instance by considering the behaviour of a model consisting of two coupled resonators. The theorem states that the sum of the numerators determining the contributions of the different absorption frequencies to the rotatory power should vanish, *i.e.*,

if

$$\rho = \sum_r \frac{a_r \nu^2}{\nu_r^2 - \nu^2}, \qquad (9)$$

then

$$\sum_r a_r = 0.$$

Proofs of this summation rule involving no special assumptions regarding the molecular model have since been given by several authors (*vide* reviews by Condon, 1937; Kauzmann, Walter and Eyring, 1940; Mathieu, 1946).

It is clear that the criterion furnished by this summation rule should be taken into account in deriving any formula, theoretical or empirical, which

claims to express rotatory dispersion. Without entering into the detailed numerical calculations, even a rough estimate of

$$\sum_r a_r \, (= \sum_r Q_r/\lambda_r^2)$$

in formulæ (1)–(8) shows *that the summation rule is far from fulfilled by any one of them.* As there is little justification in working out complicated expressions if we do not restrict ourselves to the basic requirement of the theory we may conclude that all the earlier formulæ are wholly inappropriate for the case of quartz.

A New Formula

The present writer has found (1952, 1954 *b*) that the rotatory dispersion of quartz from the visible to the extreme ultraviolet region of the spectrum is accurately represented by a simple formula involving only two constants, *viz.*,

$$\rho = \frac{k\lambda^2}{(\lambda^2 - \lambda_0^2)^2}. \qquad (10)$$

The formula approximates to Biot's Law when $\lambda \gg \lambda_0$. Also for a given value of λ_0, the rate of variation of the rotatory power with wavelength in this formula is much greater than in the Drude type of formula. The constants which the experimental data are

$$k = 7 \cdot 19, \qquad \lambda_0^2 = 0 \cdot 00858 \qquad \text{or} \qquad \lambda_0 = 0 \cdot 0926283\,\mu.$$

Here ρ is in degrees per millimetre and λ is in microns. The correct procedure is to express λ as the wavelength of light in vacuum. Servant has done so for his measurements in the remote ultraviolet, but the other authors have given the wavelengths in air. However, in the process of trying to fit a rotatory dispersion formula, Servant has effected the necessary corrections for a few wavelengths, extending from 1525 Å to 7000 Å. The rotatory powers for these wavelengths along with the values calculated with the above formula are set out below (Table I).

The agreement is very good from 6000 Å to 1525 Å. The error in this range, which never exceeds about two parts in a thousand, *is not of a progressive nature.* Data are available for many more wavelengths. The present writer (1954 *c*) has verified the validity of the formula for over 80 wavelengths extending from 6000 Å to 1520 Å. The fit is found to be extremely good over this range, the error being sometimes positive, sometimes negative. There is a slight discrepancy as we proceed towards the

TABLE I

$\lambda_{vac.}$ (in μ)	ρ (expt.)	ρ (calc.)	ρ (expt.)—ρ (calc.)
·1525	776·0	776·3	—0·3
·1550	724·0	724·1	—0·1
·1650	564·5	563·1	+1·4
·1750	453·5	453·1	+0·4
·1850	374·0	374·2	—0·2
·1950	315·5	315·3	+0·2
·2000	291·3	291·3	±0·0
·2250	205·9	205·9	±0·0
·2500	154·60	154·56	+0·04
·3000	97·72	97·61	+0·11
·4000	50·26	50·17	+0·09
·5000	30·86	30·84	+0·02
·6000	20·93	20·96	—0·03
·7000	15·13	15·20	—0·07

infrared from the red end of the spectrum. This is no doubt due to the contribution of the infrared bands which have not been included in the above formula. Lowry's measurements upto 3·7 μ definitely indicate the necessity of introducing a small infrared term.

It can easily be shown that the single characteristic wavelength at 0·0926283 μ used in the above formula lies in the region of the spectrum in which the ultraviolet bands of quartz appear. A one-term dispersion formula for the ordinary refractive index of quartz has been fitted up using this same wavelength. The formula proposed is of the Sellmeier-Drude type which is theoretically valid irrespective of whether a polarisation field exists or not (Krishnan and Roy, 1956). The formula is

$$n_\omega^2 - 1 = \frac{1 \cdot 35\, \lambda^2}{\lambda^2 - \lambda_0^2}, \qquad (11)$$

where

$$\lambda_0^2 = 0\cdot00858.$$

λ (in μ)	n_ω (expt.)	n_ω (calc.)
·18547	1·676	1·673
·20006	1·649	1·649
·21107	1·634	1·635
·2428	1·605	1·606
·3034	1·577	1·578
·3587	1·564	1·564
·4800	1·550	1·550
·5893	1·544	1·544
·7065	1·540	1·540
·8447	1·538	1·538

The agreement is reasonably good over the whole range. This indicates that the characteristic wavelength at $0\cdot0926283\,\mu$ is approximately the effective average of the absorption spectrum of quartz in the ultraviolet. Of course, it is well known that the average characteristic wavelength operative in refractive dispersion and in rotatory dispersion formulæ need not necessarily be the same, simply because the form of the expressions in the two cases are different (Condon, *loc. cit.*), but in the particular case of quartz they happen to roughly coincide.

The rotatory power normal to the optic axis was measured for the first time by Voigt (1905). There have been a number of subsequent measurements, the most recent being those of Bruhat and Weil (1936), who have summarised their results as follows: the ratio of the rotatory powers of quartz perpendicular and parallel to the optic axis is independent of the wavelength for the spectral interval 5780 Å – 2 40 Å, the ratio being—0·54 to within an accuracy of 0·5%.

Evidently, the rotatory dispersion normal to the optic axis should also be expressible by a formula of the same type as (10) with λ_0 unaltered and k reduced in the ratio of—0·54.

DISCUSSION

In their article in the *Handbuch der Physik*, Born and Goppert-Mayer (1933) arrive at the general formula

$$\rho = \sum_r \frac{P_r \lambda^2}{(\lambda^2 - \lambda_r^2)^2} + \frac{Q_r}{(\lambda^2 - \lambda_r^2)} + \sum_v \frac{P_v \lambda^2}{(\lambda^2 - \lambda_v^2)^2} + \frac{Q_v}{(\lambda^2 - \lambda_v^2)} \quad (12)$$

It will be noticed that in addition to terms of the Drude type certain quadratic terms of the same form as suggested earlier are also present. We have now discovered that these terms play a predominant role in determining the rotatory dispersion of quartz. The simplicity of the new formula and the accuracy of its fit clearly shows that terms of the Drude type do not contribute in any observable measure to the rotatory power of quartz in the visible and ultraviolet region of the spectrum.

After this work had been completed, it was found on going through some of the very early literature on the subject that in 1883 Lommel had suggested a formula of the type

$$\rho = \frac{a\lambda^2}{(\lambda^2 - \lambda_0^2)^2}$$

for quartz and a few optically active liquids. He found that the available data for quartz from 8000 Å to 2200 Å were expressed tolerably well when $\log a = 0{\cdot}8555912$ or $a = 7{\cdot}17119$ and $\log \lambda_0^2 = 7{\cdot}9341257 - 10$ or $\lambda_0 = 0{\cdot}0928032\,\mu$.

Lommel's work has apparently been overlooked by most of the authors who have since been interested in this crystal. We have now found that this formula fits the data even up to the extreme ultraviolet. In addition, as we shall see later, we have been able to give it a theoretical basis while actually Lommel's work was done before any proper theory of optical activity had yet been put forward.

THE THEORY OF COUPLED OSCILLATORS

The idea that optical activity arises from a particular spatial distribution of coupled oscillators was developed by Born, Oseen, Gray, de Mallemann and others (*vide* reviews by Condon, *loc. cit.*; Kauzmann, *et al.*, *loc. cit.*; Mathieu, *loc. cit.*). Later, Kuhn contributed greatly to the subject by putting forward a simple model which demonstrated all the essential features of the phenomenon. Kuhn's model consists of two linear anisotropic resonators having natural frequencies of free vibration ν_1 and ν_2 respectively which are coupled with each other. Each resonator

is a charged particle which is assumed to be bound elastically to its own equilibrium position and capable of vibrating along a line. The analysis shows that the system has two modes of vibration, in each of which both resonators take part, one with frequency ν_1 and the other with frequency ν_2. The contributions of the two modes to the rotatory power turn out to be of opposite signs when the frequency of the incident light is less than that of either resonator.

In this model ν_1 and ν_2 are assumed to be very different, so that the change of frequency brought about by the mutual coupling has been neglected altogether. This is, however, not permissible when ν_1 and ν_2 are very close to each other. In fact, in the limiting case when $\nu_1 = \nu_2$, each frequency is actually split into a doublet, the magnitude of the splitting being dependent on the strength of the interaction between the resonators.

We shall now discuss the optical behaviour of two identical linear anisotropic resonators coupled with each other. Let the natural frequency of vibration of the charged particle in each resonator be ν_0, when uncoupled. As a result of the coupling, ν_0 would be split into two frequencies ν_1 and ν_2. In one normal mode of vibration, the particles in the two resonators would vibrate with equal amplitude and in the same phase, and in the other normal mode they would vibrate with equal amplitude but opposite in phase.

Let the first resonator be situated at the origin of the co-ordinate system and let its vibration direction be OX. Let the second resonator be at (0, 0, d) with its vibration direction parallel to OY. Suppose the charge and mass of the particle in each resonator to be q and M respectively. For convenience, we shall put $q = fe$ and $M = fm$, where e and m are the charge and mass of the electron and f the oscillator strength. We shall call this coupled system the *compound* resonator. Let us examine the action of a light wave on such a compound resonator.

Let right circular light given by

$$x = E_0 \cos \omega t$$

$$y = -E_0 \sin \omega t$$

be incident along OZ. The force exerted by the light wave on the charged particle of the first resonator is

$$F_1 = fe\,E_0 \cos \omega t.$$

The force on the charged particle of the second resonator which is rotated through 90° about the Z axis with respect to the first one is

$$F_2 = -fe\,E_0 \sin (\omega t - \phi),$$

where

$$\phi = \frac{2\pi \bar{n} d}{\lambda},$$

$\bar{n}$ being the mean refractive index of the medium. Since ϕ is small

$$F_2 = -fe\, E_0 (\sin \omega t - \phi \cos \omega t).$$

Now, the compound resonator has two normal modes of vibration and the force may be expressed in terms of the two normal co-ordinates as

$$R_{\xi_1} = \frac{1}{\sqrt{2}} (F_1 + F_2)$$

$$R_{\xi_2} = \frac{1}{\sqrt{2}} (F_1 - F_2)$$

Substituting for F_1 and F_2, we get

$$R_{\xi_1} = \frac{fe\, E_0}{\sqrt{2}} [(1 + \phi) \cos \omega t - \sin \omega]$$

$$= a^r{}_{\xi_1} fe\, E_0 \cos (\omega t + \sigma),$$

where $(a^r{}_{\xi_1})^2 = (1 + \phi)$, neglecting higher powers of ϕ. Hence, the equation of motion of the particles would be of the form

$$\ddot{\xi}_1 + \omega_1{}^2 \xi_1 = a^r{}_{\xi_1} \frac{fe\, E_0}{M} \cos (\omega t + \sigma).$$

Therefore,

$$\xi_1 = \frac{a^r{}_{\xi_1} fe\, E_0 \cos (\omega t + \sigma)}{M (\omega_1{}^2 - \omega^2)}$$

Hence, the dipole moment induced

$$= (a^r{}_{\xi_1} fe)^2 \frac{E_0}{M (\omega_1{}^2 - \omega^2)}$$

$$= (a^r{}_{\xi_1})^2 f \frac{e^2}{m} \frac{E_0}{\omega_1{}^2 - \omega^2}$$

putting $M = fm$. The dipole moment could be expressed as two components at right angles to each other, say m_g and m_k, where

$$m_g = f \frac{e^2}{m} \frac{E_0}{\omega_1{}^2 - \omega^2}.$$

and

$$m_K = \phi f \frac{e^2}{m} \frac{E_0}{\omega_1^2 - \omega^2}.$$

These results are for a single compound resonator. If there are N such compound resonators all lying with their axes parallel to OZ but assuming different orientations about it, the mean polarisability per unit volume would be $N(m_g + m_K)/2E_0$.

Hence

$$(n_r^2 - 1)_{\xi_1} = 2\pi N (a^r_{\xi_1})^2 \frac{e^2}{m} \frac{f}{\omega_1^2 - \omega^2}.$$

In a similar manner, we get for the other normal mode

$$(n_r^2 - 1)_{\xi_2} = 2\pi N (a^r_{\xi_2}) \frac{e^2}{m} \frac{f}{\omega_2^2 - \omega^2},$$

where

$$(a^r_{\xi_2})^2 = 1 - \phi.$$

Let us write

$$n_r^2 - 1 = (n_r^2 - 1)_{\xi_1} + (n_r^2 - 1)_{\xi_2}.$$

For left circular light given by

$$x = E_0 \cos \omega t$$
$$y = E_0 \sin \omega t,$$

we have similarly

$$(n_l^2 - 1)_{\xi_1} = 2\pi N (a^l_{\xi_1})^2 \frac{e^2}{m} \frac{f}{\omega_1^2 - \omega^2},$$

$$(n_l^2 - 1)_{\xi_2} = 2\pi N (a^l_{\xi_2})^2 \frac{e^2}{m} \frac{f}{\omega_2^2 - \omega^2},$$

where

$$(a^l_{\xi_1})^2 = 1 - \phi,$$
$$(a^l_{\xi_2})^2 = 1 + \phi,$$

and

$$n_l^2 - 1 = (n_l^2 - 1)_{\xi_1} + (n_l^2 - 1)_{\xi_2}.$$

Therefore,

$$n_l^2 - n_r^2 = 4\pi N \frac{e^2}{m} f \phi \left[\frac{1}{\omega_2^2 - \omega^2} - \frac{1}{\omega_1^2 - \omega^2}\right]$$

It will be noticed that the numerators in the two terms are equal in magnitude but opposite in sign and this is in conformity with Kuhn's summation rule.

Let

$$\omega_1^2 = \omega_0^2 + 2\pi^2\epsilon$$
$$\omega_2^2 = \omega_0^2 - 2\pi^2\epsilon$$

We shall assume that the resonators are not very strongly coupled so that ϵ is a small quantity. Putting

$$n_l + n_r = 2\bar{n}, \quad \phi = \frac{2\pi\bar{n}d}{\lambda}$$

and

$$\omega_0 = 2\pi\ \nu_0,$$

we get

$$n_l - n_r = \frac{\mathrm{N}e^2 d}{m\lambda}\frac{f\epsilon}{(\nu_0^2 - \nu^2)^2}$$

neglecting ϵ^2 in the denominator. Hence

$$\rho = \frac{\pi}{\lambda}(n_l - n_r) = \frac{\mathrm{A}_0\lambda^2}{(\lambda^2 - \lambda_0^2)^2},$$

where

$$\mathrm{A}_0 = \frac{\pi \mathrm{N}e^2 d\lambda_0^4 f\epsilon}{mc^4}.$$

If the compound resonators were randomly oriented we would have to introduce a factor $\frac{1}{3}$ in the expression for the rotatory power.

If, as a more general case, we assume that the first resonator (0, 0, 0) has direction cosines α, β, γ and that the second resonator (0, 0, d) is rotated through an angle θ about the Z axis with respect to the first one, it may be shown that

$$\rho = \frac{\mathrm{A}_0\lambda^2}{(\lambda^2 - \lambda_0^2)^2}, \tag{13}$$

where

$$\mathrm{A}_0 = \frac{\pi \mathrm{N}e^2 d \sin\theta\,(\alpha^2 + \beta^2)\,\lambda_0^4 f\epsilon}{3\,mc^4}$$

It will be seen from (13) that the two enantiomorphous forms will have opposite rotatory powers, since $\rho \propto \sin\theta$,

Thus, by means of an extremely elementary model we have been able to derive the correct expression for the rotatory dispersion of quartz. It should be exphasised that the new single term formula intrinsically satisfies Kuhn's summation rule and is therefore more justified than any of the earlier formulæ worked out for this crystal.

We shall now try and interpret these results in terms of the structure of quartz. α-Quartz belongs to the space group D_3^4 or the enantiomorphous D_3^6. The unit cell has three SiO_2 units spaced at equal intervals along the vertical screw axis, each of which is turned through 120° with respect to its predecessor. It is this screw structure which is responsible for its optical activity, the individual constituent units themselves being optically inactive. In view of the foregoing theoretical considerations, it can scarcely be doubted that the rotatory power of quartz arises primarily as a result of an interaction in the nature of a resonance between the similar polarisable units constituting the crystal. This type of interaction causes a splitting of the characteristic frequency of each individual unit and consequently, the rotatory dispersion formula is of the form (13). By a simple extension of the model which we have just considered, it may be shown in an approximate way (Chandrasekhar, 1954 *c*) that for an hypothetical crystal with a screw structure built up of such compound resonators, the rotatory dispersion formula for propagation of light along and normal to the optic axis are both of the quadratic form (13), a result which agrees with the experiments of Bruhat and Weil (*loc. cit.*).

The same type of formula is also found to fit the data for cinnabar, benzil and sodium chlorate (Chandrasekhar, 1953, 1954 *a*, 1954 *c*) quite well and, in fact, much better than any of the previous formulæ proposed for these crystals. It may be remarked that, like quartz, the rotatory power of these crystals is present only in the crystalline state and not in solution.

In conclusion, I have great pleasure in expressing my thanks to Professor Sir C. V. Raman, F.R.S., for the valuable discussions I had with him during the course of these investigations. I am also grateful to Dr. S. Ramaseshan for his kind advice and interest.

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